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APPLICATION AND EVALUATION OF ANALYTICAL PROCEDURES FOR TRACE METALS, TOTAL CYANIDES AND PHENOLICS

by

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Contract No. 68-03-2788

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Analytical procedures for the determination of trace metals, total cyanide and phenolics were systematically evaluated for their applicability industry-wide. Matrix interferences, methods equivalency, and analytical precision were investigated through a series of duplicate and spiked analyses on non-diluted and diluted samples. Validation of the methodologies and identification of their limitations were thus established both within specific industrial classifications and across multiple industrial processes.

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FOREWORD

Environmental measurements are required to determine the quality of ambient waters and the character of waste effluents. The Environmental Monitoring and Support Laboratory - Cincinnati, conducts research to:

- Develop and evaluate methods to measure the presence and concentration of physical, chemical, and radiological pollutants in water, wastewater, bottom sediments, and solid waste.

- Investigate methods for the concentration, recovery, and identification of viruses, bacteria and other microbiological organisms in water, and, to determine the responses of aquatic organisms to water quality.

- Develop and operate an Agency-wide quality assurance program to assure standardization and quality control of systems for monitoring water and wastewater.

- Develop and operate a computerized system for instrument automation leading to improved data collection, analysis, and quality control.

This report evaluates analytical procedures used to determine trace metals, total cyanide and phenolics when applied to samples representative of industry-wide matrices. Interferences, method equivalency and analytical precision were investigated.

Robert L. Booth

Robert L. Booth, Acting Director
Environmental Monitoring and
Support Laboratory - Cincinnati

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ABSTRACT

Analytical procedures for the determination of trace metals, total cyanide and phenolics were systematically evaluated for their applicability industry-wide. Matrix interferences, methods equivalency, and analytical precision were investigated through a series of duplicate and spiked analyses on non-diluted and diluted samples. Validation of the methodologies and identification of their limitations were, thus, established both within specific industrial classifications and across multiple industrial processes.

Each analytical technique was affected to some degree by certain matrix interferences. Direct flame aspiration produced the most reliable results of any atomic absorption technique. Mild and vigorous digestions preceding flame aspiration were equivalent for most samples and elements. Graphite furnace and chelation/extraction procedures generally produced reliable results but were more susceptible to matrix effects than direct flame aspiration. Graphite furnace and sodium borohydride hydride generation methods for arsenic and selenium proved acceptable, whereas zinc slurry hydride generation suffered from losses during digestion. Graphite furnace and chelation extraction methods for hexavalent chromium were affected by specific interferences but each produced valid results for most samples.

The three phenolic methods tested were not equivalent and only 4-AAP colorimetric produced reasonable results. The MBTH colorimetric and instrumental methods were highly limited by severe matrix interferences or high background signals.

The pyridine pyrazolone and pyridine barbituric acid methods for total cyanide produced equivalent results and generally reliable data.

Holding times for phenolics and cyanides can be increased from 24 hours to 10 days based on preservation studies.

This report was submited under Contract No. 68-03-2788 by Biospherics Incorporated under the sponsorship of the U.S. Environmental Protection Agency. The sampling and analytical program was conducted over a 12-month period, June, 1979 - June, 1980.

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Miles Haven, Data Processing Director

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SECTION 1

INTRODUCTION

Section 304(h) of the Federal Water Pollution Control Act of 1972 requires that the Administrator of the Environmental Protection Agency promulgate guidelines establishing test procedures for the quantification of pollutants in industrial effluents. In this project, state-of-the-art analytical procedures which have been approved for trace metals, total cyanide, and phenolics effluent compliance monitoring were systematically evaluated in a wide variety of industrial effluents to assess their industry-wide applicability. Several procedures for these parameters which have not been officially approved but which show promise were also evaluated.

The state-of-the-art analytical procedures under study have generally been found to provide reliable data. However, all analytical procedures can be rendered ineffective by interferences which may be present in effluent matrices. The relative presence of these matrix interferences can vary markedly across industry in general and are affected by various wastewater treatment processes. In order to investigate the applicability of these procedures to industry in general, a wide variety of effluents representing numerous industries and industrial processes were sampled and analyzed. Procedures for metals, total cyanide and phenolics were evaluated for effluents from 24, 8 and 10 Standard Industrial Classifications (SIC), respectively, and within each of these classifications, multiple processes were sampled whenever possible. SIC Codes investigated are identified in Table 1. Samples were collected at sites which were permitted or anticipated permits to discharge the contaminant of interest. Thus, an evaluation of the analytical procedures on representative compliance samples was achieved.

Atomic absorption analytical methods were evaluated for trace metal determinations. Sample preparation, direct flame aspiration, chelation/extraction, graphite furnace, hydride generation, and mercury cold vapor techniques of atomic absorption spectroscopy were included in this investigation. Two colorimetric methods as well as an instrumental method were evaluated for phenolic determinations. A titrimetric and two colorimetric methods for total cyanide were also evaluated.

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TABLE 1. DESCRIPTION OF STANDARD INDUSTRIAL CLASSIFICATION CODES

Standard Industrial Classification Codes	Description
1061	Ferroalloy Ores, Except Vanadium
1094	Uranium-Radium-Vanadium Ores
1099	Metal Ores, Not Elsewhere Classified
2231	Broad Woven Fabric Mills, Wool (Including Dying and Finishing)
2262	Finishers of Broad Woven Fabrics of Man-Made Fiber and Silk
2269	Finishers of Textiles, Not Elsewhere Classified
2621	Paper Mills, Except Building Paper Mills
2812	Alkalies and Chlorine
2819	Industrial Inorganic Chemicals, Not Elsewhere Classified
2821	Plastics Materials, Synthetic Resins, and Non-vulcanizable Elastomers
2822	Synthetic Rubber (Vulcanizable Elastomers)
2823	Cellulosic Man-Made Fibers
2879	Pesticides and Agricultural Chemicals, Not Elsewhere Classified
2911	Petroluem Refining
3229	Pressed and Blown Glass and Glassware, Not Elsewhere Classified
3312	Blast Furnaces (Including Coke Ovens), Steel Works, and Rolling Mills
3313	Electrometallurgical Products
3315	Steel Wire Drawing and Steel Nail Spikes
3331	Primary Smelting and Refining of Copper

TABLE 1. DESCRIPTION OF STANDARD INDUSTRIAL CLASSIFICATION CODES (continued)

Standard Industrial Classification Codes	Description
3332	Primary Smelting and Refining of Lead
3333	Primary Smelting and Refining of Zinc
3341	Secondary Smelting and Refining of Nonferrous Metals
3471	Electroplating, Plating, Polishing, Anodizing and Coloring
3861	Photographic Equipment and Supplies
4911	Electric Services
9999	Mixed Domestic and Industrial Sewage Effluent (MDISE)

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Interferences, both positive and negative, as well as other procedural limitations, were investigated through a series of sample dilutions, standard additions, and multiple determinations. Preservation techniques for total cyanide and phenolics were also evaluated.

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SECTION 2

CONCLUSIONS AND RECOMMENDATIONS

TRACE METALS

Silver

Effluents from SIC 2819 and 3861 as well as mixed domestic and industrial sewage effluent (MDISE) were sampled to evaluate applicability of atomic absorption methodologies for total silver.

Silver was lost during the mild acid digestion (MAD)(1) in all samples including quality control samples prepared in deionized water. Apparently, silver precipitated or plated out on the walls of digestion beakers. This problem was overcome by diluting up the mild digest with cyanogen iodide (CNI) and ammonium hydroxide (NH_4OH)(2) which redissolved the precipitated silver resulting in good recoveries. The vigorous acid digestion (VAD)(3) was effective without requiring CNI. Equivalent results were achieved for the MAD using CNI and the VAD. Care should be taken to use the appropriate digestion protocol when analyzing for silver along with other metals. The effect of using CNI although positive for silver is unknown for other metals. Thus, if a common digest is to be analyzed for additional metals, the VAD should be used. Alternately, separate digestions are recommended. A digestion step could be eliminated for total silver determinatins by simply adding CNI/NH_4OH to a sample aliquot previously preserved in nitric acid. The entire sample could be preserved with CNI if only silver determinations were required(2). Testing to determine the applicability of substituting CNI for an acid preservative and digestion should be performed prior to the adoption of this technique.

No significant interferences were detected for direct aspiration analyses in SIC 3861 and MDISE. However, severe negative interferences were encountered in all SIC 2819 effluents resulting in silver recoveries generally below 30%. This loss of silver appeared to occur during the MAD (even though CNI was used) since spikes of the digest were recovered to nearly 100%. SIC 2819 effluents contained higher levels of dissolved salts, suspended solids, and organic matter than most other samples investigated.

Positive interferences were identified for graphite furnace analyses of samples in SIC 3861. These interferences were effectively eliminated by diluting the digested matrix. No significant interferences were detected for graphite furnace analysis of SIC 2819 or MDISE samples.

Two chelation/extration procedures produced recoveries between 70% and 130% for 21 of 28 sample spikes. The ammonium pyrrolidine dithiocarbamate/methyl isobutyl ketone (APDC/MIBK)(4) procedure generally showed lower silver recoveries than the pyrrolidine dithiocarbamic acid/chloroform ($PDCA/CHCl_3$)(5) procedure.

Aluminum

Effluents from SIC 3341 and MDISE were analyzed to evaluate direct aspiration and graphite furnace atomic absorption procedures for total aluminum. The MAD and VAD produced equivalent results for all samples analyzed. No significant interferences were identified for direct aspiration or graphite furnace techniques.

Barium

Effluents for SIC 2819 and MDISE were analyzed for total barium by direct aspiration and graphite furnace atomic absorption procedures.

Equivalent results were achieved for the MAD and the VAD.

Direct aspiration analyses for MDISE samples produced good recoveries for all sample spikes. Severe negative interferences were encountered for five of nine effluent sites in SIC 2819. As stated previously, SIC 2819 samples were relatively high in dissolved salts, solids, and organic matter.

SIC 2819 samples also exhibited interferences, both positive and negative, for graphite furnace analyses. No inerferences were noted in MDISE samples.

Cadmium

Samples from SIC 1061, 1094, 1099, 3331, 3332, 3333 and 3471 as well as MDISE were analyzed for total cadmium by atomic absorption methods to evaluate their applicability.

Equivalent results were achieved for the MAD and the VAD.

Of 54 samples analyzed by direct aspiration only two in SIC 3471 exhibited interference effects. These positive interferences were largely reduced by 1:1 dilutions.

The graphite furnace technique yielded good recoveries for all samples with the exception of those from SIC 3333 (minor positive interferences) and MDISE (moderate negative interferences). These interferences were partially or totally eliminated by 1:2 dilutions.

The PDCA/$CHCl_3$ chelation/extraction technique exhibited no interferences in any SIC code. The APDC/MIBK technique exhibited a positive interference in samples from SIC 3333. This interference was largely eliminated by a 1:2 dilution. The APDC/MIBK technique was successful for all other samples.

Chromium

Samples from SIC 2231, 2262, 2269, 2819, 2821, 2911, 3312, 3313, 3471 and MDISE were analyzed for total chromium by atomic absorption techniques. Samples from SIC 3312 and 3315 were analyzed for dissolved chromium. Samples from SIC 2819, 2911, 3312, 3313 and 3471 were analyzed for hexavalent chromium by the two chelation/extraction procedures and precipitation/graphite furnace technique.(6)

In preparing samples for total chromium analysis, significant chromium was lost (>50%) during the VAD from samples containing <0.5 mg/l in SIC 2911 and MDISE. The percentage loss relative to the MAD decreased for higher concentrations. The apparent loss of chromium could have been due to a negative interference enhanced by the VAD rather than actual chromium loss. Equivalent chromium results for the VAD and MAD were achieved at all concentrations for other SIC Codes.

No significant interferences were noted in any sample from any SIC Code analyzed for total chromium by direct aspiration.

The graphite furnace technique for total chromium was successful on 22 of 25 samples analyzed. Negative interferences were identified in one sample from SIC 2231 (6% recovery) and two samples from SIC 2269 (68% and 54% recoveries). Sample dilutions (1:2) improved these recoveries to acceptable limits.

The 30-minute permanganate digestion time preceding chelation/extraction techniques for total chromium was found insufficient to convert trivalent chromium to the hexavalent state. The digestion time was increased to 4 hours resulting in complete oxidation and thus good extraction efficiencies. Many samples contained matrices which destroyed permanganate resulting in a heavy brown precipitate. Large amounts of permanganate were thus required for some digestions. Often it was difficult to determine if an excess of permanganate was present due to the dark precipitate. A 4-hour digestion time probably incorporated a large safety margin and can probably be significantly reduced for

most samples. The digestion efficiency should be checked with trivalent chromium sample spikes and reference analyses to verify that the digestion time used is sufficient for oxidation to occur.

The APDC/MIBK chelation/extraction method for total chromium yielded recoveries between 70% and 130% for 39 of 46 sample spikes. Only occasional positive interferences were encountered. The PDCA/$CHCl_3$ method produced 70% - 130% recoveries for 43 of 46 sample spikes. A 4-hour digestion time was used for all analyses.

All methods produced satisfactory results for all samples analyzed for dissolved chromium.

Interferences affecting hexavalent chromium procedures were present in a small percentage of samples in SIC 2819, 2911, 3312, 3313 and 3471. These interferences were specific to particular sites or samples and not widespread throughout the industries. Interferences in SIC 2819 affected all three methods (APDC/MIBK, PDCA/$CHCl_3$, furnace), however, in all other cases their effects were limited to either both chelation/extraction procedures or the furnace method. For samples where interferences were not encountered, the furnace technique produced better recoveries than either chelation/extraction method. In addition, the detection limit of the furnace method is 5X better than the chelation/extraction methods.

Interferences occurring in both chelation/extraction procedures were often visually noted by the formation of a pronounced black precipitate upon chelate addition. Formation of this extractable precipitate can be used to predict interferring effects for hexavalent chromium and other trace metals. Abnormalities in the normal hexavalent chromium precipitation pattern used in conjunction with the furnace procedure were also noticed in some samples producing interferences. For instance, a heavy precipitate was formed in some SIC 2819 samples when lead nitrate was added to precipitate the hexavalent chromium. This precipitation could indicate that the lead nitrate was consumed before hexavalent chromium could be precipitated. Thus, these observations can be used to flag potential methodology problems.

The furnace procedure for hexavalent chromium is the most cost-effective method from a labor and materials basis.

Copper

Effluents from SIC Codes 1061, 1099, 2819, 3331, 3341, 4911 and MDISE were analyzed by atomic absorption procedures for total copper. Samples from SIC 3315 were analyzed for dissolved copper.

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The VAD produced up to 40% higher total copper results than the MAD for samples from SIC 1061 and 2819. The digestion procedures correlated to within ± 5% for all other samples containing significant amounts of copper.

No significant interferences were identified for any sample analyzed for total copper by direct aspiration techniques.

Of 24 samples analyzed for total copper by graphite furnace, 23 produced copper spike recoveries between 70% and 130%.

Each chelation extraction procedure yielded total copper recoveries between 70% and 130% for 43 of 48 sample spikes.

Good recoveries were achieved for SIC 3315 samples analyzed for dissolved copper by direct aspiration and chelation/ extraction procedures. Positive interferences affected graphite furnace analyses resulting in 150% recoveries.

Iron

Effluents from SIC 1099, 2819, 4911 and MDISE were analyzed for total iron by atomic absorption methods. SIC 3312 and 3315 samples were analyzed for dissolved iron.

The VAD often gave 10% - 40% higher total iron results than the MAD, particularly for samples high in suspended solids such as those from SIC 4911.

Direct aspiration analyses for total iron produced recoveries between 70% and 130% for 180 of 190 sample spikes. SIC 2819 samples which contained higher levels of particulate matter showed relatively poorer recoveries than other samples.

In all SIC Codes 26 of 36 spikes were recovered between 70% and 130% when analyzed for total iron by the graphite furnace technique. Poor recoveries appeared to be due to variable efficiencies of the MAD used in conjunction with the furnace procedure (See Section 7, Discussion).

The APDC/MIBK chelation/extraction procedure for total iron produced 24 of 36 spike recoveries in the 70% - 130% range. The PDCA/$CHCl_3$ procedure yielded 27 of 36 spikes recovered in the same range.

No interferences were identified in any sample analyzed for dissolved iron by the direct aspiration and chelation/extraction procedures as 65 of 66 spikes were recovered between 85% and 115%. Success of these dissolved iron determinations confirmed the digestion step to be the deciding factor for total iron analytical success.

Graphite furnace analyses for dissolved iron were affected by negative interferences in some SIC 3312 and 3315 samples. These interferences were eliminated by 1:2 dilutons.

Iron is a common element of particulate matter in many industrial effluents. Consequently, the precision of sample aliquotting and MAD efficiencies is a greater limitation for iron determinations than for other elements typically in the soluble state. Many apparent interferences affecting total iron were due to these limiting factors rather than actual matrix interferences.

Mercury

Samples from SIC 1099 and 2812 were analyzed by the cold vapor atomic absorption technique for total mercury.

Recoveries between 70% and 130% were achieved for 23 of 36 sample spikes. SIC 2812 samples from 3 of 8 sites produced recoveries below 55% (see Section 7, Discussion).

Manganese

Samples from SIC 3312, 3313 and MDISE were analyzed by atomic absorption methods for total manganese.

The VAD gave up to 27% higher results than the MAD, however, most results agreed to within $\pm$ 10% or better.

No significant interferences were identified for direct aspiration, graphite furnace, or PDCA/$CHCl_3$ chelation/extraction techniques.

A standard curve could not be achieved for manganese determinations by the APDC/MIBK chelation/extraction method. Apparently the manganese complex was not sufficiently stable. Samples and standards were run within 30-60 minutes of chelation, thus, the complex, if formed, breaks quickly as no absorption was noted during aspiration.

Nickel

Effluents from SIC 1099, 2819, 3471 and MDISE were analyzed for total nickel by atomic absorption methods. Samples from SIC 3312 and 3315 were analyzed for dissolved nickel.

The VAD and MAD produced equivalent results.

Flame conditions were critical for total nickel determinations in the direct aspiration technique. An oxidizing flame must be maintained as recoveries of 170% were noted for quality

control samples when using even a slightly rich flame. With an oxidizing flame all 72 spikes were recovered between 70% and 130% with 70 of 72 recovered between 85% and 115%. Nickel was the only metal which was consistently and successfully determined on SIC 2819 samples.

Graphite furnace analyses for total nickel produced 16 of 18 spike recoveries between 70% and 130%.

No interferences were identified for either chelation/extraction technique for total nickel.

No significant interferences affecting dissolved nickel results were identified for direct aspiration or the PDCA/$CHCl_3$ chelation/extraction technique. One of five samples exhibited a moderate negative interference by the graphite furnace procedure. The APDC/ MIBK procedure was successful on nine of ten samples with one sample showing a moderate negative interference effect.

Lead

Effluents from SIC 1061, 1099, 2812, 3229, 3312, 3332 and MDISE were analyzed for total lead by atomic absorption procedures.

The VAD and MAD produced equivalent results.

All 144 spikes in the seven industrial categories analyzed by direct aspiration were recovered between 85% and 115%. The furnace procedure produced 26 of 32 recoveries between 70% and 130%. The PDCA/$CHCl_3$ and APDC/MIBK chelation/extraction procedures produced 31 of 32 and 28 of 32 recoveries in the 70% to 130% range, respectively.

Only SIC 1099 samples were problematic for furnace and chelation/extraction procedures as negative interferences produced low recoveries. Dilutions remedied difficulties for the chelation/extraction methods, however, furnace recoveries remained below 30%.

Tin

Effluents from SIC 3312, 3471 and MDISE were analyzed for total tin by direct aspiration and graphite furnace atomic absorption procedures.

The VAD and the MAD produced equivalent results at flame levels (>0.5 mg/l) when hydrochloric acid (HCl) was used. Without HCl, precipitation of tin occurred in both reference and effluent samples resulting in low recoveries. Thus, HCl must be

utilized in digestions for tin determinations. Tin, when present at furnace levels (<0.1 mg/l), was lost during the MAD even with 2% HCl. The VAD was not studied at furnace analytical levels.

By using HCl in the MAD all 64 sample spikes were recovered between 70% and 130% with 62 of 64 recovered between 85% and 115%.

Furnace analyses produced consistently low recoveries due to tin precipitation in the MAD. Unacceptable recoveries resulted for both reference and effluent samples. Thus, losses could not be attributed to matrix effects. The applicability of the VAD should be studied at furnace levels, and if problems exist an alternate digestion procedure should be developed for tin.

Zinc

Effluents from SIC 1061, 1094, 2621, 2823, 3312, 3331, 3332, 3333, 3341 and MDISE were analyzed for total zinc by atomic absorption procedures.

The VAD yielded results lower than the MAD for SIC 1094 samples. The methods were equivalent for all other samples.

Direct aspiration analyses were quite successful, producing recoveries between 70% and 130% for 164 of 172 spikes.

Graphite furnace determinations for zinc were susceptable to severe laboratory contamination problems. The extreme sensitivity of the method and the prevalence of zinc in the laboratory environment necessitated the use of extraordinarily meticulous analytical technique to achieve reliable results. The relative abundance of zinc in reagents, glassware and other experimental materials created the potential for severe zinc contamination problems by the furnace method. Meticulous cleaning procedures and reagent purification was applied for low level zinc concentrations with limited success. The potential for introduction of gross contamination during sample injection into the furnace was high. Automated sample injection introduced unacceptable zinc contamination into the furnace. Manual injection when carefully controlled produced adequate results for most samples, however, occasional contamination during injection was unavoidable.

Contamination was also a problem for zinc by the chelation/extraction methods.

It is doubtful that zinc would ever have to be detected in effluents at chelation/extraction and furnace levels (0.5-5 ug/l). Therefore, direct aspiration which is not severely

affected by zinc contamination problems is recommended for routine analyses. If the furnace technique is used for specialized analyses when low detection limits are required, manual furnace injection should be used instead of auto-injection which was a high contributor to contamination. The analyst's technique should be refined and investigated to ensure proper furnace injection procedures.

Arsenic

Effluents from SIC 1061, 1094, 2819, 3331, 3333 and MDISE were analyzed for total arsenic by graphite furnace as well as sodium borohydride and zinc slurry hydride generation techniques of atomic absorption spectrophotometry.

The graphite furnace technique using nickel as a matrix modifier produced 89 of 108 spike recoveries in the 70% to 130% range. Moderate positive interferences affected SIC 3333 sample analyses and severe negative interferences were encountered in SIC 2819 samples. Despite these interferences, the furnace method produced superior results to either hydride generation method.

The sodium borohydride hydride generation technique produced recoveries between 70% and 130% for SIC 1061, 3331, 3333 and MDISE samples. Positive interferences were encountered in SIC 1094 and severe negative interferences were again encountered in SIC 2819.

The zinc slurry method of hydride generation was limited by losses in the digestion procedure, inconsistencies of the standard curves, and contamination of zinc powder. Poor resutls were obtained for all SIC Codes.

Selenium

Effluents from SIC 2819, 3331, 3333 and MDISE were analyzed for total selenium by graphite furnace as well as sodium borohydride and zinc slurry hydride generation techniques of atomic absorption spectrophotometry.

The graphite furnace technique proved quite successful for SIC 3331, 3333 and MDISE samples yielding 33 of 36 spike recoveries in the 70% to 130% range. However, as with most other metals, severe negative interferences were encountered for SIC 2819 samples.

The sodium borohydride hydride generation technique also produced acceptable results for all samples except those of SIC 2819.

Similarly as for arsenic, the zinc slurry method produced poor recoveries for the majority of samples.

General

Effluents from SIC 2819 were the most problematic of any industrial category sampled. Interferences affected chromium, hexavalent chromium, iron, silver, copper, barium, arsenic and selenium determinations. Only nickel was determined with consistent reliability. Relatively high levels of dissolved and suspended solids as well as organic matter in samples from this category were probably responsible for method problems.

The MAD or the VAD can be used interchangeably for most samples and elements. The VAD should be more effective for samples high in particulate iron. The MAD is quicker, less labor intensive, and not susceptible to VAD errors introduced by sample spattering or baking when approaching dryness.

The formation of a black precipitate upon chelate addition should be used as an indicator of possible negative interferences for the chelation/extraction procedures. Sample spikes should be taken through the procedure to investigate the interference effect. If the interference is significant a sample dilution should be made and the chelation/extraction performed again with and without spikes. An alternate method (direct aspiration or furnace) should be used if problems cannot be overcome by reasonable dilutions.

With the exception of a few techniques (zinc slurry for arsenic and selenium, APDC/MIBK for manganese, MAD for tin) each of the analytical procedures is capable of delivering reliable results for industrial effluent monitoring. However, each method also has certain limitations and can be adversely affected by specific matrix interferences. Several analytical options are available for most elements. The method of choice will depend on required detection limits, susceptibility to interferences, cost-effectiveness, complexity, and other factors. Preferably, the method chosen should be the simplest one available which produces reliable results and meets detection limit requirements. The method, therefore, will be cost-effective and reliable. For example, the direct aspiration technique is least susceptible to interferences and is also the quickest and most cost-effective method available. Its levels of detection are generally poorer than other methods, but if they are adequate to meet permit guidelines, direct aspiration would be the method of choice.

Evaluating analytical methods as performed by use of reference samples and spikes should be used as a routine quality control check for analytical programs.

CYANIDES

Total cyanide was determined by the pyridine barbituric acid (PBA) colorimetric method, the pyridine pyrazalone colorimetric (PPC)(7) method and the silver nitrate titrimetric (TTM)(7) method on samples from SIC 1099, 2819, 3312, 3313, 3315, 3471, 3861 and MDISE. All analyses were preceded by the sulfuric acid/magnesium chloride distillation procedure.(7)

The PBA procedure produced recoveries between 70% and 130% for 136 of 164 sample spikes. Interferences were identified in a small percentage of samples from SIC 2819, 3312, 3313 and 3315.

The PBA and the PPC procedures produced equivalent results for sample concentrations and precision. Both methods were affected similarly by the few interferences which were encountered. These methods can thus be used interchangeably.

The TTM procedure also proved effective showing good precision and spike recoveries. Negative interferences were identified in one SIC 3312 sample.

Samples preserved with sodium hydroxide (NaOH) and stored at $4^{o}C$ showed no significant loss of cyanide over a 10-day study period. However, only a limited data base from two SIC Codes was accumulated.

PHENOLICS

Phenolics were determined by the 4-amino antipyrine (4-AAP) colorimetric method, the 3-methyl-2-benzothiazolinone hydrazone hydrochloride (MBTH)(9) colorimetric method and the PH-3 instrumental method (PHI)(10) on samples from SIC 2231, 2262, 2491, 2821, 2879, 2911, 3312, 3313, 3861 and MDISE. All methods were preceded by a distillation.(8)

The 4-AAP colorimetric method produced recoveries in the 70% - 130% range for 186 of 256 sample spikes. The 4-AAP method was less susceptible to interferences than the MBTH colorimetric or the PHI instrumental method.

Significant interference effects were encountered in all SIC Codes for MBTH as only 112 of 256 spikes were recovered in the 70% - 130% range. A green or blue colored complex possibly due to aldehyde reactions often formed instead of the characteristic pink phenolic complex.

The PHI method produced only 64 of 256 spike recoveries in the 70% to 130% range. This method was severely affected by

large background readings relative to actual phenolic response. These background levels were not reproducible between distillations which further impacted reliability. An alternate sample preparation method should be developed for use with the phenol instrument. Solvent extraction followed by back extraction into water may be a possibility.

The three methods did not produce equivalent results. PHI phenolic determinations were often an order of magnitude greater than the colorimetric methods due to PHI positive interferences as well as limitations on the phenolic reactivity of 4-AAP and MBTH. When interferences were absent the MBTH method generally produced higher results than 4-AAP, thus MBTH is probably reactive with a greater variety of phenolic compounds than 4-AAP. Method precision and interference effects also were not equivalent for the three methods.

No significant loss of phenolics occurred over a 10-day preservation period for eight of nine samples from different SIC Codes preserved with phosphoric acid or sulfuric acid and copper sulfate. The remaining sample produced variable results due to an interfering matrix. Small phenolic increases with time occurred for some samples possibly due to changes in phenolic substitution increasing reactivity with 4-AAP. Based on these results from eight industrial effluents, phenolic samples which have been preserved with phosphoric or sulfuric acid and copper sulfate and refrigerated to 4°C can be stored for at least 10 days prior to analysis.

Ferrous ammonium sulfate used to destroy oxidizing agents was ineffective in removing the final traces from the effluent samples. Excesses also produced a yellow tint to some distillates which posed a potential interference with the 4-AAP yellow complex. An alternate substance, possibly ascorbic acid, should be investigated as a substitute for ferrous ammonium sulfate.

SECTION 3

ANALYTICAL PROGRAM

Tables 2 and 3 summarize analytical procedures which were evaluated in this project. Each procedure was systematically evaluated through a series of spikes, dilutions and replicate analyses to investigate precision, accuracy, equivalency, and susceptability to positive and negative interferences. The evaluation protocols for all parameters are described below.

TRACE METALS

Methods of Atomic Absorption Spectroscopy (AAS) were evaluated for the determination of trace metals. The analytical protocols shown in Tables 4-11 at the end of this section were completed for each AAS method. The basic analytical protocol for AAS procedures is summarized as follows: (a) initial analyses were performed in duplicate, (b) duplicate sample aliquots were spiked prior to processing (digesting, etc.) processed and analyzed, (c) duplicates from the original processed sample were combined, diluted in duplicate, and analyzed, (d) duplicate sample aliquots from the combined duplicates of the original processed sample were diluted, spiked and analyzed.

The basic analytical protocol was designed to:

- identify samples with interferring matrices and identify techniques susceptible to interferences
- evaluate recoveries from sample preparation techniques
- evaluate precision of the analytical technique

Matrix interferences can be identified from spike recoveries and confirmed by dilution analyses. A low or high recovery of undiluted sample spikes may indicate the presence of a negative or positive interference. The possible presence of an interference can be confirmed by comparing correlation of the diluted analysis to the original undiluted analysis since interferences seldom reflect the actual dilution factor. The spike of the dilution can further confirm the presence of an interference

Table 2. Trace Metals Procedures

Atomic Absorption Techniques	Al	Ag	As	Ba	Cd	Cr	Cr VI	Cu	Fe	Hg	Pb	Mn	Ni	Se	Sn	Zn
Flame Aspiration	X	X		X	X	X		X	X		X	X	X		X	X
Vigorous Digestion	X	X		X	X	X		X	X		X	X	X		X	X
Mild Digestion	X	X		X	X	X		X	X		X	X	X		X	X
Filtration						X		X	X				X			
Chelation Extraction		X			X	X		X	X		X	X	X			X
Vigorous Digestion		X			X			X	X		X	X	X			X
Filtration						X	X	X	X				X			
Permanganate Digestion						X										
PDCA/$CHCl_3$		X			X	X	X	X	X		X	X	X			X
APDC/MIBK		X			X	X	X	X	X		X	X	X			X
Graphite Furnace	X	X	X	X	X	X	X	X	X		X	X	X	X	X	X
Mild Digestion	X	X		X	X	X		X	X		X	X	X		X	X
Peroxide Digestion			X											X		
Chromate Precipitation							X									
Hydride Generation			X											X		
Zn Slurry/Sulfuric Digestion			X											X		
$NaBH_4$/Permanganate Digestion			X											X		
Cold Vapor										X						
Permanganate Digestion										X						

Digestions - Total Metals

Filtration - Dissolved Metals

Reference - Methods for Chemical Analyses of Water and Wastes, EPA-600 4-79-020, 1979.

TABLE 3. CYANIDE AND PHENOLIC PROCEDURES

Parameter	Analytical Method
Total Cyanide	Sample Prep - H_2SO_4, $MgCl_2$ Reflux Distillation, NaOH trapping (7)
	Analysis by Pyridine Pyrazolone Colorimetric (7)
	Pyridine Barbituric Acid (7) Colorimetric
	Silver Nitrate Titration (7)
Phenolics	Sample Prep - Distillation
	Analysis by 4 - Amino Antipyrine Colorimetric (4-AAP)(8)
	3 - Methyl-2-Benzothiazolinone Hydrazone Hydrochloride Colorimetric (MBTH)(9)
	PH-3 Instrumental (10)

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since the diluted spike should be recovered to the same degree or closer to 100% than the original undiluted spike. An example of this logic is expressed below:

- o original analysis yields 10 mg/l
- o 10 mg/l spike into the undiluted sample yields 15 mg/l or only a 50% recovery of the spike, thus a possible negative interference exists
- o 1:1 dilution of original processed sample yields 7 mg/l equivalent to 14 mg/l when the dilution factor is applied. Negative interference has been confirmed and at least partially diluted out
- o 15 mg/l spike of the diluted aliquot yields 20 mg/l for a recovery of 87%: 20-7 = 13 as recovery of the spike (13/15)(100) = 87% recovery. Matrix interference was diluted out to yield higher recovery.

The sample processing or preparation technique can be evaluated from spikes of the original undiluted sample. A low recovery from spiked original samples may indicate loss in the sample preparation process particularly if the correlation of diluted sample values to original sample values is good and the spike recovery of the diluted processed sample shows no sign of a negative interference.

The precision of the analytical technique can be estimated based on duplicate ranges. Precision as a function of SIC Code, industrial process, and concentration can be evaluated.

The effectiveness of a mild (MAD) versus a vigorous (VAD) acid digestion were compared by flame aspiration. Different analytical techniques used to measure common analytes were evaluated for equivalency based on the original analysis, relative precision and susceptability to interferences.

Each method was evaluated for precision by analyzing seven replicates from samples in a detectable analytical range.

CYANIDES

The analytical protocol for total cyanide is shown in Table 12. The pyridine barbituric acid procedure(7) was employed for samples having less than 1 mg/l cyanide and the titrimetric method(7) on samples greater than 1 mg/l. The pyridine pyrazolone method(7) was used on all spiked 1:1 dilutions under 1 mg/l to determine method equivalency. Duplicate distillates were run

for all samples throughout the analytical scheme. Samples were analyzed by the appropriate procedure as received with and without spike, and diluted 1:1 with and without spike. Interferences were detected by computing spiked recoveries of original and diluted samples and by comparing results from sample dilutions with undiluted samples.

Precision studies were performed on several samples by multiple determinations. The possibility of increasing holding times was evaluated by performing a series of 10-day preservations studies.

PHENOLICS

Analytical protocols for phenolics are shown in Table 13. The 4-AAP(8) and instrumental methods(10) were run on common distillates from samples preserved with phosphoric acid. The MBTH method(9) was run on samples preserved with sulfuric acid. Duplicate analyses were performed on common distillates rather than single analyses performed on duplicate distillates. When extraction procedures were performed, 200 ml aliquots diluted to 500 ml were taken for analysis. Samples were analyzed as received with and without spikes, and diluted 1:1 with and without spikes.

Precisison and preservation studies were run similarly as for cyanides.

TABLE 4. TRACE METALS PROTOCOL 1

Flame Aspiration/MAD with HCl

1. Digest original preserved samples in duplicate. Analyze each duplicate.

2. Spike original preserved samples in duplicate for each metal to 1.5X or 2X original concentration, digest and analyze.

3. Dilute combined digests from Step 1 in duplicate 1:1 with deionized water acidified to same concentration as sample aliquot and analyze.

4. Dilute combined digest as in Step 3 in duplicate adding a spike for each metal to achieve final concentration as in Step 2 and analyze.

NOTES: Follow similar protocol for dissolved metals substituting filtrations for digestions.

If metals not detected spike to 10-15X 1% absorption.

TABLE 5. TRACE METALS PROTOCOL 2

Flame Aspiration/VAD

1. Based on results of Protocol 1, rank sites within SIC from highest to lowest concentration for each metal using the highest sample concentration at each site. For SIC's with only 1 site, rank samples from high to low concentration for each metal.

2. Based on the ranking in Step 1, perform VAD in duplicate on the higher one-third of samples (a minimum of 2).

3. Analyze by flame aspiration.

NOTES: Eliminate this protocol for dissolved metals.

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TABLE 6. TRACE METALS PROTOCOL 3

Graphite Furnace/MAD without HCl

1. Rank sites within each SIC similarly as in Protocol 2 but based on lowest sample concentrations at each site.

2. Based on ranking in Step 1, perform MAD in duplicate on the lower one-third of samples (a minimum of 2) and analyze. Digest and analyze all arsenic and selenium samples using peroxide digestion.

3. Spike the preserved samples to 1.5X or 2X the original concentration for each metal. Digest in duplicate and analyze.

4. Combine the duplicate digests in Step 2 and dilute in duplicate 1:2 with 0.5% nitric acid in deionized water and analyze.

5. Dilute the combined digests as in Step 4 in duplicate adding a spike for each metal to achieve a final concentration as in Step 3 and analyze.

NOTES: Follow similar protocol for dissolved metals substituting filtrations for digestions.

Follow similar protocol for hexavalent chromium using the chromate precipitation pretreatment. Analyze all samples.

If metals not detected spike to 10-15X 1% absorption.

HCl was used for tin in the MAD.

TABLE 7. TRACE METALS PROTOCOL 4

Chelation/Extraction/VAD

1. Use the VAD and run in duplicate the original preserved samples chosen in Protocol 3. For total chromium use the permanganate digestion. For hexavalent chromium, filter only and analyze all samples.

2. Extract each duplicate by APDC/MIBK and PDCA/$CHCl_3$ and analyze extracts.

3. Spike the preserved samples to 1.5X or 2X the original concentration of each metal. Digest in duplicate, extract by both methods and analyze.

4. Dilute combined digests from Step 1 in duplicate 1:2 with deionized water acidified to same concentration as sample aliquot. Extract by both methods and analyze.

5. Dilute combined digests as in Step 4 spiking each metal to final concentration in Step 3. Extract by both methods and analyze.

NOTES: Follow similar protocol for dissolved metals substituting filtration for digestions.

TABLE 8. TRACE METALS PROTOCOL 5

Zinc Slurry Hydride Generation

1. Digest original preserved samples in duplicate with sulfuric/nitric acids and analyze by zinc slurry hydride generation.

2. Spike original preserved samples to 2X or 1.5X original concentration. Digest in duplicate and analyze.

3. Dilute combined digests in Step 1 in duplicate 1:1 with acid diluent and analyze.

4. Dilute as in Step 3 in duplicate adding spike to achieve a final concentration as in Step 2, and analyze.

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TABLE 9. TRACE METALS PROTOCOL 6

$NaBH_4$ Hydride Generation

1. Digest one preserved sample in duplicate from each site requiring As or Se by permanganate digestion and analyze.

2. Digest in duplicate a 1.5X or 2X spike of that sample and analyze. If originally undetected spike to 0.01 mg/l.

TABLE 10. TRACE METALS PROTOCOL 7

Mercury Cold Vapor

1. Digest preserved samples in duplicate and analyze.

2. Spike samples to 1.5X or 2X the original concentration, digest in duplicate, and analyze. Spike to 0.002 mg/l if undetected.

3. Dilute combined digests in Step 1 in duplicate 1:1 with deionized water acidified similarly as the sample, and analyze.

4. Dilute combined digest in duplicate as in Step 3 adding a spike to achieve a final concentration as in Step 2.

TABLE 11. TRACE METALS PROTOCOL 8

Precision Statement

1. Flame Aspiration/MAD-Analyze seven replicates for three samples for each element at different concentrations.

2. Zinc Slurry Hydride Generation; Graphite Furnace; Cold Vapor; Hexavalent Chromium Extractions-Analyze seven replicates for two samples at different concentrations.

3. Extraction Methods for other metals. Analyze seven replicates from one sample.

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TABLE 12. TOTAL CYANIDE PROTOCOL 9

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1. Distill samples in duplicate. Analyze by titration if over 1 mg/l. Analyze by pyridine barbituric acid (PBA) colorimetric method if under 1 mg/l.

2. Spike sample with 100 ug/l if original concentration is <1 mg/l or with 1 mg/l if original concentration is >1 mg/l. Distill in duplicate and analyze by PBA or titration.

3. Dilute sample 1:1, add spike as in step 2, distill in duplicate and analyze by PBA or titration.

4. Dilute sample 1:1, add spike as in step 2, distill in duplicate and analyze by PBA and pyridine pyrazolone colorimetric method (PPC) or titration.

5. Determine precision by analyzing seven replicates from each of two samples from SIC 3312, 2819, 3313, 3315 and 3861.

6. Analyze one sample in duplicate on ten consecutive days from SIC 3312, 3313, 3315, 3861 and 1099 to evaluate preservation techniques.

TABLE 13. PHENOLICS PROTOCOL 10

1. Distill samples preserved with phosphoric or sulfuric acids and $CuSO_4$. Analyze phosphoric distillate by 4-AAP and PHI in duplicate. Analyze sulfuric distillate by MBTH in duplicate.

2. Spike samples with 25 ug/l if original concentration is less than 50 ug/l or spike with 100 ug/l if higher than 50 ug/l. Distill and analyze in duplicate by MBTH or 4-AAP and PHI as applicable.

3. Dilute samples 1:1, distill and analyze in duplicate.

4. Dilute samples 1:1, add appropriate spike, distill and analyze in duplicate.

5. Determine precision by analyzing six samples from SIC 2911, 3312, 2821, 2231 and 3313 seven times each.

6. Analyze by 4-AAP one sample from each SIC in duplicate on ten consecutive days to evaluate the preservation technique.

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SECTION 4

SAMPLING PROGRAM

A listing of industries identified for sampling, as well as the number of sites and samples taken are provided in Tables 14, 15, and 16. SIC Code identification is provided in Table 17. Identification of permit holders, gaining permission to sample eligible sites, sample collection, preservation and delivery to the laboratory for analysis were major functions of the sampling program.

Grab samples were collected according to "Sampling Water and Wastewater," EPA, 1977 and preserved according to the 1979 EPA "Manual for Chemical Analysis of Water and Wastes."

Grab samples were collected directly from end of pipe outfalls via hand operated pumps, impellor pumps, direct bottle collection, or submersible grab sampling equipment. Samples from common sites were collected at least 3 hours apart.

Trace metal samples were collected in 4-liter polyethylene "cubitainers" and preserved with nitric acid to achieve a final concentration of 0.5% resulting in a pH <2. These samples were stored at room temperature.

Cyanide samples were collected in 10 liter polyethylene "cubitainers" and preserved with 10 ml of 10 N sodium hydroxide to a pH >12. Prior to preservation oxidizing agents were destroyed with ascorbic acid. Samples were kept at 4°C.

Phenolic samples were collected in 4-liter amber glass containers. Oxidizing agents were destoryed with an excess of ferrous ammonium sulfate. The sample was then split in two parts. One part was preserved with phosphoric acid and copper sulfate and the second was preserved with sulfuric acid and copper sulfate. Each sample was stored at 4°C.

Sampling sites were categorized by SIC Code and a process description is presented in Table 17 and Appendix III. Samples were usually collected from sites which had, or were in anticipation of, National Pollutant Discharge Elimination System (NPDES) permits to discharge the analyte under study. Discharge permit parameters for each site are also tabulated in Appendix III.

TABLE 14. TRACE METALS
SAMPLING STRATEGY

SIC Code	Number of Sites Sampled	No. of Samples Collected At Each Site For: Total Metals	Hexavalent Chromium	Dissolved Metals	Total Number of Samples Collected	Required Analyses for: Total Metals	Dissolved Metals	Hexavalent Chromium
1061	1	6	--	--	6	As, Cd, Cu, Pb, Zn	--	--
1094	6	2	--	--	12	As, Cd, Zn	--	--
1099	1	6	--	--	6	Cd, Cu, Fe, Pb, Hg, Ni	--	--
2231	6	2	--	--	12	Cr	--	--
2262	4	2	--	--	8	Cr	--	--
2269	4	2	--	--	8	Cr	--	--
2621	5	2	--	--	10	Zn	--	--
2812	6	2	--	--	12	Pb, Hg	--	--
2819	9	2	2	--	36	As, Ba, Cr, Cu, Fe, Ni, Se, Ag	--	Cr^{+6}
2821	7	2	--	--	14	Cr	--	--
2823	4	2	--	--	8	Zn	--	--
2911	14	2	2	--	56	Cr	--	Cr^{+6}
3229	8	2	--	--	16	Pb	--	--
3312	10	2	2	2	60	Cr, Pb, Mn, Sn, Zn	Cr, Fe, Ni	Cr^{+6}
3313	4	2	2	--	16	Cr, Mn	--	Cr^{+6}
3315	4	--	--	2	8	--	Cr, Cu, Fe, Ni	--
3331	1	6	--	--	6	As, Cd, Cu, Se, Zn	--	--
3332	1	6	--	--	6	Cd, Pb, Zn	--	--
3333	2	3	--	--	6	As, Cd, Se, Zn	--	--
3341	2	3	--	--	6	Al, Cu, Zn	--	--
3861	4	2	--	--	8	Ag	--	--
4911	33	2	--	--	66	Cu, Fe	--	--
MDISE	1	6	--	--	6	Al, Ag, As, Ba, Cd, Cr, Cu, Fe, Pb, Mn, Ni, Se, Sn, Zn	--	--
3471	2	3	3	--	12	Cd, Sn, Cr, Ni	--	Cr^{+6}
				TOTAL	404			

TABLE 15. TOTAL CYANIDE

SAMPLING STRATEGY

SIC Numbers	Number of Sampling Sites Sampled	Number of Samples Collected at Each Site	Total Number Samples Per SIC
3312	10	2	20
2819	10	2	20
3313	6	2	12
3315	5	2	10
3861	3	2	6
1099	1	6	6
MDISE	1	6	6
3471	2	3	6
		Total Number Samples	86

TABLE 16. PHENOLICS

SAMPLING STRATEGY

SIC Numbers	Number of Sites Sampled	Number of Samples Per Site	Total Number of Samples Per SIC Code
2911	14	2	28
3312	10	2	20
2821	7	2	14
2231	6	2	12
3313	6	2	12
2262	6	2	12
2879	5	2	10
2491	4	2	8
3861	1	6	6
MDISE	1	6	6
		Total Number of Samples	128

TABLE 17. DESCRIPTION OF STANDARD INDUSTRIAL CLASSIFICATION CODES

Standard Industrial Classification Codes	Description
1061	Ferroalloy Ores, Except Vanadium
1094	Uranium-Radium-Vanadium Ores
1099	Metal Ores, Not Elsewhere Classified
2231	Broad Woven Fabric Mills, Wool (Including Dying and Finishing)
2262	Finishers of Broad Woven Fabrics of Man-Made Fiber and Silk
2269	Finishers of Textiles, Not Elsewhere Classified
2621	Paper Mills, Except Building Paper Mills
2812	Alkalies and Chlorine
2819	Industrial Inorganic Chemicals, Not Elsewhere Classified
2821	Plastics Materials, Synthetic Resins, and Non-vulcanizable Elastomers
2822	Synthetic Rubber (Vulcanizable Elastomers)
2823	Cellulosic Man-Made Fibers
2879	Pesticides and Agricultural Chemicals, Not Elsewhere Classified
2911	Petroluem Refining
3229	Pressed and Blown Glass and Glassware, Not Elsewhere Classified
3312	Blast Furnaces (Including Coke Ovens), Steel Works, and Rolling Mills
3313	Electrometallurgical Products
3315	Steel Wire Drawing and Steel Nail Spikes

TABLE 17. DESCRIPTION OF STANDARD INDUSTRIAL CLASSIFICATION CODES
(continued)

Standard Industrial Classification Codes	Description
3331	Primary Smelting and Refining of Copper
3332	Primary Smelting and Refining of Lead
3333	Primary Smelting and Refining of Zinc
3341	Secondary Smelting and Refining of Nonferrous Metals
3471	Electroplating, Plating, Polishing, Anodizing and Coloring
3861	Photographic Equipment and Supplies
4911	Electric Services
9999	Mixed Domestic and Industrial Sewage Effluent (MDISE)

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SECTION 5

DATA PRESENTATION

Results for duplicate analyses of the original, diluted, and spiked samples along with calculated mean, range, and spike recovery are presented in Appendix II, Raw Data Tables.

Manipulation of these raw data to evaluate a) spike recovery of original and diluted sample aliquots, b) diluted sample analysis correlation to original analysis, c) equivalency of digestion techniques, and d) technique equivalency for various metals, phenolics and cyanide determinations are presented as Appendix I.

Recoveries are totalled as a distribution over three specific ranges which are multiples of ±15%. Good recoveries represent those between 85% and 115%. Fair recoveries are defined as those between 70% and 84% as well as 116% and 130%. Poor recoveries are those between 55% and 69% as well as 131% and 145%. Recoveires in two outlier ranges (<55% and >145%) were also totalled. The recovery distribution is segregated by a) technique, b) original spike and c) dilution spike. The recovery distribution is summed over all SIC Codes for each procedure.

Dilution versus original analyses are evaluated by comparing agreement over four correlation ranges, a) ±15%, b) ±30%, c) ±45%, and d) >±45%. Results for each analyte are compared for each SIC Code and then summed.

Both range and actual concentration are compared for the two digestion procedures for applicable trace metals. Actual mean concentration of original analyses are listed side by side for each metal. The range of the means are computed and the ratio (VAD/MAD) of the results are also listed. The range between duplicates within each digestion procedure are also listed in this table to compare precision.

Methods comparison tables for total cyanide, metals and phenolics list actual concentration for each method with ratios for cyanide and phenolics.

A detailed key and description of each data set is provided as an introduction to the Appendices. Methods of calculation are also provided.

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SECTION 6

QUALITY ASSURANCE

Comprehensive programs for quality assurance were followed throughout this project. Analytical methodologies were standardized at project initiation. Programs to ensure the integrity of instrumentation, facilities, labware, reagents, and data handling were maintained. Samples were collected, received, analyzed, and stored under chain of custody guidelines and standardized laboratory operating procedures. Quality assurance monitoring for the analytical and data handling programs are described below.

TRACE METALS

With the receipt of samples from each SIC code, one internal quality control sample per 10 samples received from that SIC Code was prepared containing all analytes of interest. Quality control samples were analyzed according to the same protocols as the samples including all dilutions, spikes, and processing. In addition, a reagent blank was analyzed with all sample sets.

An unprocessed (undigested) internal quality control sample was analyzed with a frequency of one per twenty analyses for all elements. External samples from EPA EMSL QA Branch, Cincinnati and EPA Region III were analyzed periodically during the project.

A five-point standard curve was prepared with each set of analyses. A high or low standard was run alternately every seven analyses. If more than $\pm$5% variation occurred, the entire standard curve was rerun.

CYANIDES

A high and low standard was distilled and analyzed with every set of 10 analyses. An internal quality control sample was also run with every 20 determinations. External samples from EPA EMSL QA Branch, Cincinnati were also analyzed.

A five point standard curve was run with each set of samples received. This curve was verified with two standards on each set of analyses. A new standard curve was run if variation of more than $\pm$5% occured with any two check standards.

PHENOLICS

Two internal quality control samples were distilled and analyzed with every 20 determinations. External samples from EPA EMSL QA Branch, Cincinnati were also run. A five point standard curve was run with each set of samples and verified with all sets of analyses by two standards. If these standards varied by more than ±5% from the five point curve, a new curve was run.

RESULTS

Data for quality control samples are presented with the raw data in Appendix II. Analyses of these samples proved invaluable in discovering procedural difficulties such as a) lack of silver recovery without CNI in the digest, b) low tin recovery without HCl in the digest, c) loss of recovery in digestion but not in spikes of predigested samples for arsenic and selenium (Zinc Slurry Hydride), d) phosphoric acid interferences with MBTH phenolic determinations. Matrix interferences and other difficulties in sample analyses were also confirmed by the success of matrix-free quality control analyses for deionized water control samples.

DATA HANDLING AND MANAGEMENT

Data handling and management were automated for this project, with significant attention paid to quality assurance measures. Concern for quality assurance is reflected in the forms used for transmitting data, the mechanism (punch cards) for data entry to the computer, and in the design of the software package used in handling data.

A single laboratory data recording form was utilized for each of the two basic sample types, trace metals and cyanides/phenolics. Examples of these forms are shown in Figures 1 and 2, respectively. Calculations of mean, range, sample concentration and spike recovery were performed by laboratory personnel. Codes for sample type, analyte, sample preparation and technique as identified in Appendix II were entered on the forms. Use of a single form for transmitting data from the laboratory to a keypunch service minimized the opportunity for transcription error. Completed sets of data forms were reviewed for completeness and accuracy, and then delivered to a keypunch service. The keypunch service accuracy proved to be better than 99.5%. The software developed to process and retrieve the data was designed and coded to operate within the IBM 370MVS systems currently being used by the Washington Computer Center (WCC) COMNET system. The programs for editing the raw data and subsequent formatting were written

FIGURE 1

BIOSPHERICS INCORPORATED
LABORATORY DATA CODING FORM – EPA/MCP
TRACE METALS

ANALYTICAL TECHNIQUE _____

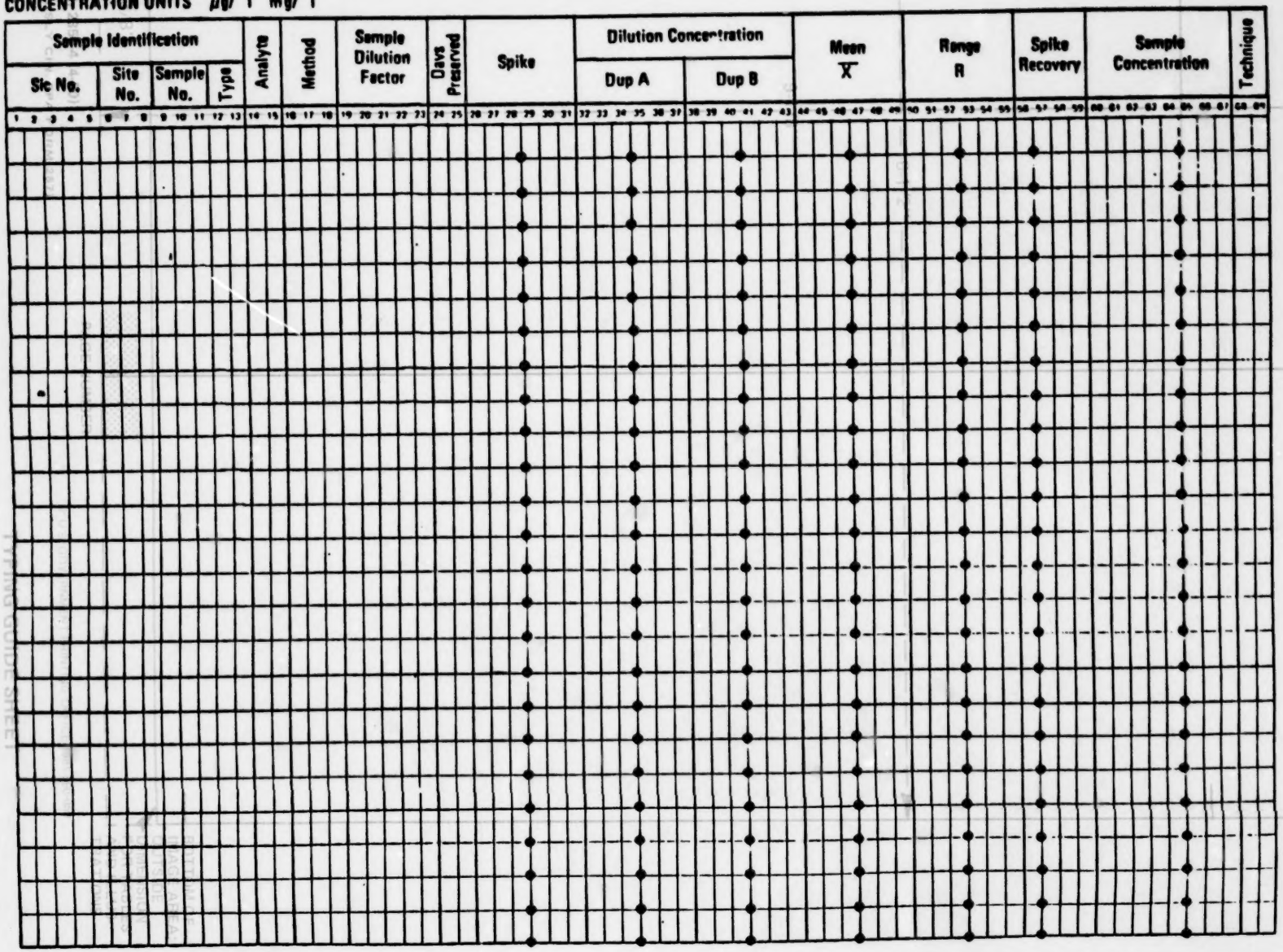
CONCENTRATION UNITS µg/l mg/l

Sample Identification				Analyte	Sample Prep	Dilution Factor		Spike	Dilution Concentration		Mean $\bar{X}$	Range	Spike Recovery	Sample Concentration	Technique
Sic No.	Site No.	Sample No.	Type			Sample	Digest		Dup A	Dup B					
1 2 3 4 5	6 7 8	9 10 11 12 13		14 15	16 17 18	19 20 21 22 23	24 25	26 27 28 29 30 31	32 33 34 35 36 37	38 39 40 41 42 43	44 45 46 47 48 49	50 51 52 53 54 55	56 57 58 59	60 61 62 63 64 65 66 67	68 69

FIGURE 2

BIOSPHERICS INCORPORATED
LABORATORY CODING FORM – EPA/MCP
PHENOLICS AND CYANIDES

PARAMETER _____
CONCENTRATION UNITS µg/ l mg/ l

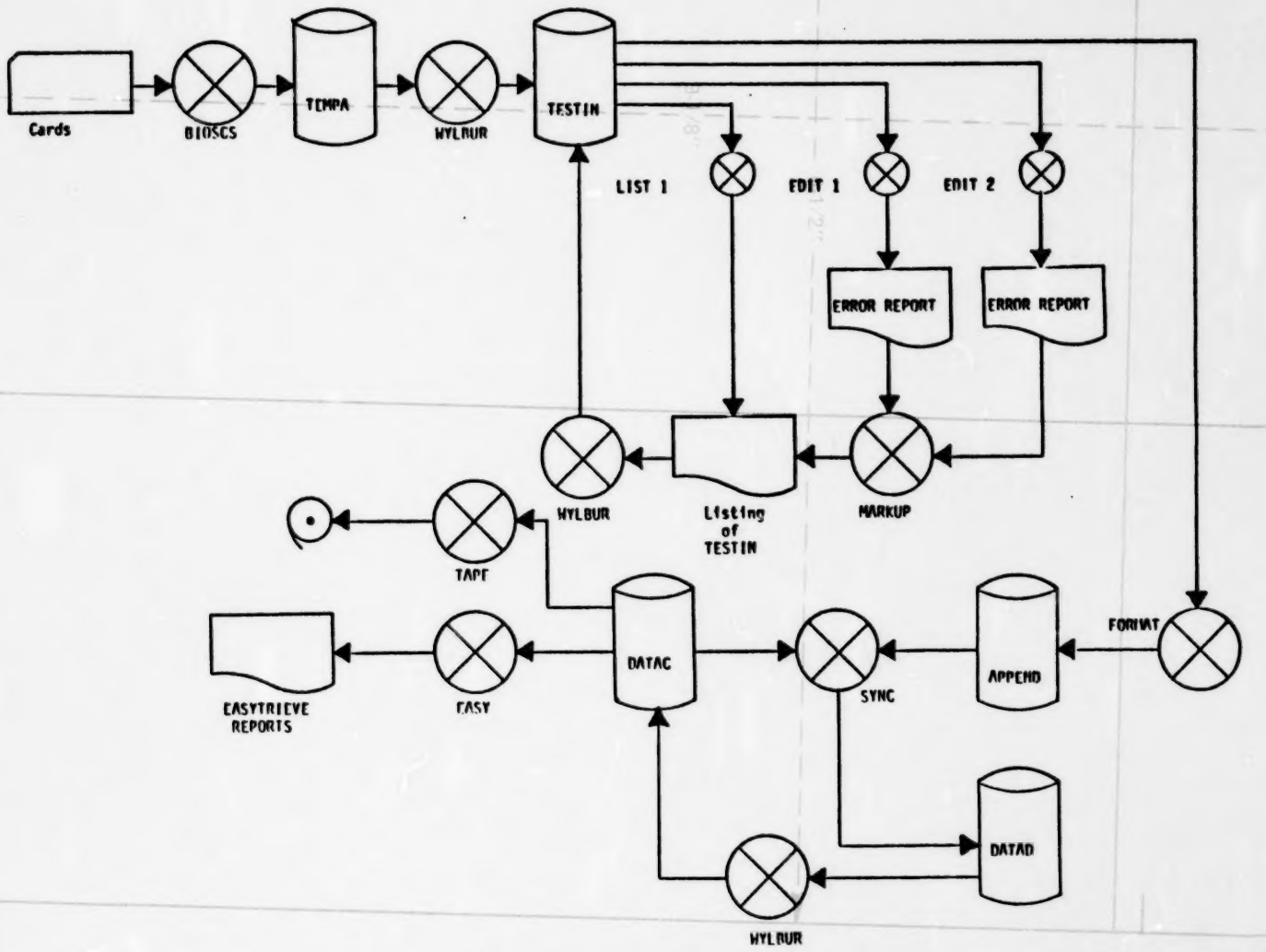


in Fortran IV GI. Data manipulation and output formats were conducted using Pansophic's EASYTRIEVE (1979), an information retrieval and data management system.

A flow chart for the data management developed for this project is presented in Figure 3. The programs provided a series of multiple checks for the data.

Data read from punch cards were entered into a temporary data base. Two editing programs, Edit 1 and Edit 2 were run on this data in succession. Edit 1 primarily checked for valid entry codes while Edit 2 checked for computation errors and the proper sequence of data. Lists of the error codes and their description produced by Edit 1 and Edit 2 are presented in Tables 18 & 19, respectively. Edit 1 was run and rerun on the data set until all entry errors were corrected. After the Edit 2 error report showed complete absence of computational errors in the data set, the data were entered into the permanent data base (DATAC). Data were added to the permanent data in a cumulative manner throughout the course of the project. The final data were manipulated into report tables using the EASYTRIEVE system. As a precaution against loss of the data through computer malfunction, a tape copy of the permanent data base was made each time a significant amount of data was added.

FIGURE 3



DATA HANDLING AND MANAGEMENT SYSTEM

EPA Contract No. 68-03-2788

TABLE 18. - EDIT 1 CODES

Code	Description
1	Not a valid SIC code
2	Site field has a non-numeric character
3	Sample number is blank or contains a non-numeric (other than blank)
4	Columns 5 or 11 is/are not blank
5	The type code is not valid for the type of form (metals or phenolics/cyanides)
6	The analyte code is not valid for the type of form
7	The sample code is not valid for the type of form
8	The sample dilution is partially blank or has a non-numeric character
9	The digest dilution or days preserved is partially blank or has a non-numeric character
10	Spike contains embedded blanks, non-numeric character or contains numerics, but none in columns 28 and 29
11	Dup a is blank or contains embedded blanks, non-numeric character(s) (other than -), or contains numerics but none in columns 34 and 35
12	Dup b is blank or contains embedded blanks, non-numeric character(s) (other than -), or contains numerics but none in columns 40 and 41. No error if field is blank and record is for AC, blank, or precision
13	Mean is blank or contains embedded blanks, non-numeric character(s) (other than -) or contains numerics but none in columns 46 and 47. No error if field is blank and record is for precision study

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TABLE 18. EDIT 1 CODES

Code	Description
14	Range is blank or contains embedded blanks, non-numeric character(s) or contains numerics but none in columns 52 and 53. Error if there was no dup b value and range contains characters
15	Spike recovery has non-numeric character(s) or embedded blanks
16	Concentration contains non-numeric character(s) embedded blanks, or contains numerics but none in columns 64 and 65
17	Technique code is not valid for form type
18	Units code is not M or U
19	Spike has value but recovery is blank or visa versa - also error if recovery has value for precision records. For QC, error if spike or concentration is blank
20	Both spike and concentration have values or both are blank. For precision error if concentration is blank. For QC, error if spike or concentrations is blank
21	Site number is not 999 for QC and Blank record

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TABLE 19 - EDIT 2 ERROR CODES

Code	Description
1	Indicates record has a spike when it should not or visa versa - out of sequence
2	Mean is incorrect
3	Range is incorrect
4	Error in sample dilution or digest dilution
5	Concentration is incorrect
6	Spike recovery is incorrect
99	Record is out of order

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SECTION 7

DISCUSSION

TRACE METALS

Data tables containing results for duplicate analyses with calculated mean, range, and spike recoveries are presented in Appendix II, along with the quality control results. Reduced data tables are presented in Appendix I. Data have been manipulated to present the following relationships:

- o spike recovery by range (Tables 1-20)
- o diluted processed sample result in comparison to the original analysis (Tables 21-40)
- o digestion comparison (Tables 41-52)
- o method equivalency (Tables 53-71)
- o method precision (Tables 72-110)

The following sections describe results for each metal.

Silver

Loss of silver during the MAD was immediately noted from the analysis of quality control samples prepared in deionized water. To verify this loss, a standard curve was put through the MAD and compared to undigested standards. As seen from results in Table 20 silver was lost from standards. Apparently, precipitation or plating of the silver on beaker walls was responsible for this loss. The use of CNI and NH_4OH(2) was implemented following the MAD during final sample workup (dilution to volume) resulting in acceptable recoveries. This procedure was standardized throughout the project and all MAD data presented was derived using CNI. The VAD was successful for quality control samples without use of CNI.

Care should be taken to use the appropriate digestion protocol when analyzing for silver along with other metals. The effect of CNI addition although positive for silver is unknown for other metals. Thus, if a common digest is to be analyzed for silver and other metals, the VAD should be used. Alternately, separate digestions are recommended.

TABLE 20. SILVER LOSS DURING MAD WITHOUT CNI

Silver Standard (mg/l)	Absorbance	
	Digested	Undigested
4	0.017	0.253
3	0.004	0.197
2	0.005	0.136
1	---	0.069

Good recoveries were achieved for the direct aspiration technique for 20 of 28 spike analyses in SIC 3861 and MDISE. The remaining eight spikes for these categories were recovered in the fair range. No significant recovery differentials were observed between spiked samples and spiked digested dilutions (1:1). Twelve of fourteen 1:2 dilution analyses agreed to within ±15% of the original sample analysis. Only one dilution result for SIC 3861 varied by more than ±30% of the original sample analysis. Since this sample contained silver at a level near the flame detection limit, a ±30% variation is not significant.

A severe negative interference was encountered in SIC 2819 for the direct aspiration technique. All 18 spiked samples put through the MAD procedure were recovered below 55%. Conversely, good recoveries were achieved on 17 of 18 spikes of the diluted digest, with the remaining spike recovered in the fair range. Thus, silver was lost for SIC 2819 samples during the MAD even with CNI/NH_4OH addition. These samples were quite high in dissolved salts as noted from flame color and shape distortion during aspiration. In addition, several sites contained high levels of organic matter or sludge.

As seen in Appendix I similar results were generally achieved by both the VAD and MAD followed by direct aspiration. In three samples, silver was detected at low levels using the MAD with CNI while no detectable silver was observed by the VAD without CNI. However, since the silver concentrations were near the detection limit no definite conclusions can be drawn. Good digestion correlation was achieved with quality control samples.

Recoveries in excess of 145% resulted from SIC 3861 sample spikes analyzed by the graphite furnace technique. Recoveries

for spiked digest dilutions did not exceed 117%. In addition, diluted analyses showed proportionately lower results than the original analyses. Thus, a positive interference appears to have been identified in this effluent category. However, it should be noted that as seen in Appendix II (Raw Data Tables), the precision of the original analysis was quite poor (±50%), yet the precision of the spiked sample, the diluted digest, and the diluted digest spike was excellent. Thus, calculations of spike recovery on the original sample may suffer from lack of precision in the original duplicate analyses. Two explanations are possible for the poor precision of the original silver analyses. First, since silver tends to precipitate as the halides, homogeneous aliquotting of particulate silver may not have been achieved. Secondly, CNI workup of samples may not be as efficient or consistent for low level silver samples. In either case, precision of the 1:2 dilutions (spiked or unspiked) would not have been affected since they were prepared from the combined original digested duplicates. Since the precision of these duplicates was good, the instrumental contribution to variation was small, whereas, the sample preparation contribution could have been significant.

Results for MDISE graphite furnace analyses showed all 12 spike recoveries in the good or fair ranges (6 of 12 in the good range) with good correlation between diluted and original sample values.

Good recoveries were achieved for all 13 original sample spikes in SIC 2819. However, only 50% - 60% recoveries were achieved for spikes of the 1:2 digested dilutions.

The chelation/extraction techniques were performed on the same VAD digests. Fair recoveries were achieved for both MDISE samples by the PDCA/$CHCl_3$ technique, and good correlation resulted between diluted and original analyses. One MDISE original sample spike analyzed by APDC/MIBK showed a recovery of <55%. The diluted digest spike was recovered to a significantly greater degree than the original sample spike, thus a definite negative interference existed in this sample affecting the APDC/MIBK technique. A similar negative interference for APDC/MIBK was identified in one SIC 3861 sample. A recovery of only 2% was achieved for the original sample spike, whereas a 57% recovery resulted from the dilution spike. The unspiked diluted sample result confirmed the negative interference by yielding a concentration of 2.5X higher than the original analysis. The PDCA/$CHCl_3$ extraction technique yielded recoveries of 62.6% and 136.5% for the original and dilution spikes of this same SIC 3861 sample. The second SIC 3861 sample yielded nearly 100% recoveries by APDC/MIBK and fair recoveries (118% - 125%) by PDCA/$CHCl_3$. Good or fair recoveries were achieved for all SIC 2819 spikes by both extraction methods which indicates that the VAD was successful where the MAD with CNI failed.

Precision for silver determinations by direct aspiration were ±1.0% for all three samples at 0.5, 1.0, and 2.0 mg/l. Furnace precisions of ±33% and ±4% were achieved for samples at 50 and 60 ug/l. Precision for a single sample at 45 ug/l was ±51% and ±8% for APDC/MIBK and PDCA/$CHCl_3$ chelation/extraction procedures, respectively.

Aluminum

Good recoveries were achieved for all direct aspiration analyses of MDISE samples. Dilution analyses were all with ±15% of the original analyses. Good recoveries were achieved for graphite furnace analyses as well. The furnace analyses of the 1:2 digest dilutions were only half of expected values based on the original analyses. However, the dilutions resulted in concentrations near the detection limit and decreased accuracy is to be expected at low level concentrations.

The direct aspiration technique produced good recoveries for all three samples from site 002 in SIC 3341. However, a negative interference was identified in site 001 as noted by poor recoveries (between 65% and 70%) for original sample and diluted digest spikes. Marginal increases (∿5%) in spike recoveries were achieved in diluted digests over the original sample. Graphite furnace determinations produced two good and two poor (138%) recoveries.

No aluminum was detectable by direct aspiration in MDISE and SIC 3341 site 001 using either digestion procedure. SIC 3341, site 002 was found to contain 1300 ug/l by the MAD and 1800 ug/l by the VAD which is within 500 ug/l, the detection limit. MAD and VAD results for quality control samples correlated to within ±9%.

Direct aspiration precisions were ±2.4%, ±2.6%, and ±15% for samples at 18, 50, and 75 mg/l. Graphite furnace precisions of ±9.6% and ±7.3% were achieved for samples at 43 and 185 ug/l.

Barium

Direct aspiration analyses of MDISE samples resulted in good recoveries for all sample spikes. No detectable barium was found at flame levels in either the original or dilution analyses. The graphite furnace technique produced good or fair recoveries for all sample spikes, and dilution to original analysis correlations were at least within ±30%.

Severe negative interferences were encountered for direct aspiration analyses in sites 001, 002, 006, 007,and 008 of SIC 2819. Original sample spike recoveries approaching 0% were achieved for all 10 samples from those five sites. Good diluted digest spike recoveries were achieved for sites 002 and 007, however, diluted digest spikes for sites 001, 006, and 008 remained low. Sites 006 and 008 were high in organics, salts and/or sludges. Good recoveries were achieved for the other four sites (eight samples).

Positive interferences affected graphite furnace analyses in sites 007 and 009 of SIC 2819 and a negative interference was identified in site 002. The original sample spikes were recovered in excess of 145% or below 55%. The interferences were reduced in the 1:2 dilutions with good recoveries achieved in two of the three samples. The interferences were confirmed by the unspiked diluted digests yielding lower or higher results than the original analyses.

No barium was detected by direct aspiration in MDISE and SIC 2819, sites 006 and 008 using either digestion procedure. The sample from site 002, SIC 2819, was found to contain 800 ug/l by the MAD and 600 ug/l by the VAD which is a good correlation considering that the detection limit is 100 ug/l. Quality control samples agreed to within ±7% and ±25% for two samples. The VAD suffered from lower precision which may be associated with varying final acid concentrations.

Precisions of ±20%, ±57% and ±71% were achieved for direct aspiration on three samples in SIC 2819. These analyses suffered from the severe interferences associated with SIC 2819 samples and, therefore, the precision is not indicative of that obtainable from samples without interferring matrices. Furnace precisions were ±21% and ±27% on SIC 2819 samples containing 150 and 350 ug/l.

Cadmium

All spike recoveries for SIC 1061, 1094, 1099, 3331, 3332, 3333, and MDISE samples were in the good range for the direct aspiration technique. Excellent correlation also existed between dilution and original analyses. Good recoveries were also achieved for four of six samples in SIC 3471. One SIC 3471 sample from site 002 exhibited a positive interference with a 186% recovery for the original sample spike and a 144% recovery for the diluted digest spike. The remaining sample from site 002 had a 137% recovery for the original sample spike and a 54% recovery for the diluted digest spike. This sample was found to contain 5 ug/l by the original analysis, however, the 1:1 dilution was found to contain 862 ug/l.

The graphite furnace technique yielded good recoveries and good dilution correlation for SIC 1061, 1094, 1099, 3331, 3332, and 3471. However, furnace recoveries of only 50% - 65% were achieved for MDISE for both original and dilution spikes. Somewhat higher results were achieved for MDISE dilutions than for original analyses, thus, a negative interference was identified in MDISE for furnace. Original analyses of two SIC 3333 samples resulted in spike recoveries of 118% and 138%. Dilution spikes were recovered to nearly 100%.

A definite positive interference was identified in SIC 3333 for the APDC/MIBK technique. Original sample spike recoveries of 332% and 214% were achieved relative to reccveries of 150% and 136% for dilution spikes. The same sample digest analyzed by PDCA/$CHCl_3$ yielded virtually 100% spike recoveries. No other interferences were identified in any SIC Code for either extraction/chelation technique.

The digestion procedures produced results agreeable to within at least 20% for all samples.

Direct aspiration precisions were $\pm$3.4%, $\pm$2.1%, and $\pm$1.6% for samples of 0.06, 1.0, and 0.6 mg/l. Furnace precisions of $\pm$13% and $\pm$11% were achieved on samples of 3 and 9 ug/l. Precision of $\pm$2.8% was achieved for both chelation/extraction methods.

Total Chromium

Of 256 spikes in 10 industrial categories 213 were recovered in the good range with all but one of the remaining spikes recovered in the fair range for the direct aspiration technique. Thus, no severe interferences were encountered. A small interference was noted in one sample from site 006, SIC 2819 where the original sample spike was recovered to 63% with the diluted spike recovered to 95%. The second sample at the same site exhibited no interference. Good correlation between original and diluted determinations was achieved for all analyses except those marginally above detection limits.

Determinations by the furnace technique yielded 38 of 50 good spike recoveries with all but four of the remaining spikes recovered in the fair range. A negative interference was identified in SIC 2231, site 006 where the original spike was recovered to only 6% and the diluted spike to 114%. A milder negative interference was also identified in SIC 2269 where original spikes were recovered at 68% and 54% with marginally higher recoveries for diluted digest spikes.

The 30-minute permanganate digestion time preceeding chelation/extraction techniques was found insufficient to convert

trivalent chromium to the hexavalent state. Quality control samples and digested standards exposed to permanganate for 30 minutes yielded no absorption when extracted and analyzed. The digestion time was increased to four hours resulting in complete oxidation and good analytical recoveries. Insufficient sample was available to repeat MDISE determinations, thus, no data is available.

The APDC/MIBK chelation/extraction technique produced good recoveries for 24 of 46 spikes and fair recoveries for an additional 15 spikes. The remaining seven spikes were all recovered over 130%, thus occasional positive interferences were encountered. However, these apparent interferences may be due to random error rather than an interfering sample matrix since a) often the diluted digest spike was recovered higher than the original sample spike, and b) the diluted analysis correlated with the original analysis.

The PDCA/$CHCl_3$ chelation/extraction technique yielded good recoveries for 29 of 46 spikes and fair recoveries for an additional 14 spikes. One sample in SIC 2821 exhibited a negative interference as noted by original and diluted digest spike recoveries of 30%. No significant interferences were noted on any of the other eight industrial categories.

Significant variations resulted between the VAD and MAD for MDISE and SIC 2911 samples. For all samples in these categories containing <0.5 mg/l chromium by MAD, the VAD resulted in concentrations of only 11% to 60% of MAD, thus significant chromium was lost in the VAD. As concentrations increased correlation improved. One sample (SIC 2911 009 02) containing 3.5 mg/l chromium by MAD yielded 2.9 mg/l by VAD, thus, only a 17% relative loss. Equivalent results were achieved for other SIC Codes on samples containing <0.5 mg/l except for those marginally above the detection limit (0.05 mg/l). Quality control samples prepared in deionized water at 3 and 5 mg/l yielded VAD to MAD correlation within $\pm$2%.

Precisions by direct aspiration of 1.6%, 1.9% and 3.0% were achieved for three samples from different SIC Codes at 1.3, 4.6, and 7.8 mg/l. Graphite furnace precisions were $\pm$26.2% and $\pm$12.5% for samples at 37 and 68 mg/l. The APDC/MIBK technique yielded precision of $\pm$17.6% at 36 mg/l while the PDCA/$CHCl_3$ technique produced $\pm$16.6% at 34 mg/l.

Dissolved Chromium

Dissolved chromium determinations were performed on samples from SIC 3312 and 3315 by filtration through 0.45u membrane filters. Direct aspiration yielded good recoveries for 52 of

56 spikes and fair recoveries for the remaining four. Similar results were achieved for all other techniques as no interferences were identified. For all four techniques, 77 of 86 spikes were recovered in the good range with the remaining 9 spikes recovered in the fair range. Good dilution to original analysis correlation was also achieved.

Hexavalent Chromium

The graphite furnace method for hexavalent chromium yielded good recoveries for 105 of 160 determinations. Twenty-two of the remaining 55 spikes were recovered between 70% and 130%. Samples from sites 001, 006, and 008 in SIC 2819 contained a negative interference with recoveries ranging from 0% - 70%. Site 006 contained a large amount of sludge which was removed by filtration as well as high levels of dissolved salts. Site 008 contained a viscous organic material orange in color. Normally a precipitate fell with the addition of acetic acid and ammonium sulfate. No precipitation occurred for site 008 samples. Site 006 samples formed a heavy precipitate after the addition of lead nitrate. Normally little or no precipitation occurred during this step.

Negative interferences were also encountered in the following samples:

- SIC 2911, Site 004; 58% - 65% recoveries
- SIC 3312, Site 006; Original sample spike recovery of 14%, diluted digest spike recoveries of 36% and 54%
- SIC 3313, Site 005 - 0% recoveries
- SIC 3471, Site 002 - 0% recoveries

In each case, all samples collected at the above sites were affected by the interference.

Severe negative interferences were encountered for both chelation/extraction techniques for sites 006 and 008 in SIC 2819 and sites 002, 006, and 007 (sample 1) in SIC 3313, and sites 009 and 013 in SIC 2911. Without exception these samples turned deep black with the addition of the chelating agent. The black substance was extracted into the chloroform layer. The chelating agent was obviously affected by the sample matrix inhibiting its ability to chelate chromium. However, good recoveries were achieved on two samples which also blackened. The samples with interfering matrices from SIC 2819 contained high amounts of organic materials as described above. Separated oil was present in sites 009 and 013 of SIC 2911. Thus, the presence of organic

substances may be responsible for the noted interferences. In any case, the formation of a black chelate represented a flag indicating possible negative interferences.

The interferences in SIC 2819 (sites 006 and 008) and SIC 3312 (site 006) affected all three methods. However, the remaining interference effects were limited to either the furnace or the chelation/extraction methods. Thus, for most samples at least one of the methods proved reliable. It is difficult to assess the reducing potential of the sample matrix which could have resulted in formation of trivalent chromium causing low recoveries. This effect may be a factor for those samples whose matrices interfered with all three procedures. However, the critical step most susceptible to matrix interferences appeared to be the formation of the chelate (extractions) or the precipitate (furnace). Matrices which inhibit these processes will cause low recoveries, whereas interferences during instrumental detection are not key factors. Unusual reactions during these steps should be noted and spike recoveries examined before data is accepted as valid.

For samples where severe interferences were not encountered, the furnace technique produced a larger percentage of good recoveries than the chelation/extraction methods. The furnace technique had roughly a 5X better detection limit. Precision was between $\pm$2.5% and $\pm$7.5% for all three methods when interferences were absent.

The furnace procedure is the most cost effective method from a labor and materials basis. The chelation/extraction procedures require bulky volumetric glassware or separatory funnels. The use of solvents mandates that the extraction procedures be conducted in hoodspace. Conversely, the furnace method requires only small 15 ml centrifuge tubes and a centrifuge. The extraction procedures, thus, occupy several feet of hood space, whereas, the furnace method occupies the space for a centrifuge and test tube rack. The PDCA/$CHCl_3$ method is particularly time consuming with several tedious pH adjusments and several 2-minute separatory funnel extractions which become exhausting in a large scale analytical production-type situation.

Total Copper

All 190 spikes for samples in SIC 1061, 1099, 3331, 3341, 4911, and MDISE were recovered in the good range by direct aspiration. Some very minor positive and negative interferences were noted in SIC 2819, however, even in this effluent 34 of 36 spikes were recovered in the good or fair range.

Graphite furnace analyses produced 38 of 48 spikes recovered in the good range and eight of the remaining 10 recovered in the

fair range. A positive interference was identified in one sample from site 007, SIC 2819 showing an original sample spike recovery of 170% and a diluted digest spike recovery of 150%.

The extraction procedures also produced generally good results. Good recoveries were achieved for 37 of 48 spikes by APDC/MIBK, with six of the remaining 11 spikes recovered in the fair range. Samples from SIC 4911 produced most of the poor recoveries and occasional minor positive or negative interferences were encountered.

The VAD produced about 40% higher results than the MAD for both SIC 1061 samples analyzed at a concentration roughly 5X higher than the 0.020 mg/l detection limit. Higher VAD results were also achieved for two SIC 2819 samples from sites 006 and 008. These samples contained large amounts of sludge and organic matter. All other samples correlated to at least within $\pm$5% except those approaching the detection limit.

Flame precisions of $\pm$3.0%, $\pm$18.7%, and $\pm$2.1% were achieved for samples containing 0.5, 1.65, and 2.1 mg/l. Furnace precisions of $\pm$4.3% and $\pm$1.6% were obtained for samples of 0.02 and 0.7 mg/l. Precision for APDC/MIBK of $\pm$2.9% was achieved at a concentration of 240 mg/l while PDCA/$CHCl_3$ produced $\pm$2.2% for the same sample.

Dissolved Copper

Samples from SIC 3315 were analyzed for dissolved copper. Direct aspiration produced good recoveries for all spikes. A positive interference producing recoveries of about 150% affected graphite furnace determinations for both samples analyzed. Good recoveries were achieved for both chelation/extraction procedures.

Total Iron

No interferences affecting direct aspiration were identified in SIC 1099 or MDISE as 24 of 25 spikes were recovered in the good range. A negative interference was encountered in SIC 2819, site 007, sample 1 resulting in recoveries of <50%. A higher percentage of fair or poor recoveries were achieved for SIC 2819 samples than for the other SIC codes. Recoveries on samples from SIC 4911 were in the good range for 117 of 130 spikes with an additional eight in the fair range. High recoveries were noted in site 016 sample 1 and site 019 samples 1 and 2 for the original sample spikes. Spiked diluted digests were recovered near 100%, however, a positive interference cannot be confirmed because the diluted digest analysis correlated well with the original analysis. Iron is often present as particulate matter, thus, some of the poor or fair recoveries noted in SIC 2819 and

SIC 4911 may have been due to problems associated with homogeneous aliquotting of sample, or particulate iron digestion efficiencies rather than positive or negative matrix interferences.

Apparent positive interferences were identified in SIC 1099 samples analyzed by graphite furnace. Original sample spikes were recovered to 140% with diluted digest spikes recovered at 90% - 95%. However, diluted unspiked analyses were roughly 30% higher than the original analyses which would indicate a negative interference. Thus, the aliquotting of particulate iron and precision in the digestion efficiency of particulate iron may be the overriding factors for analytical precision and accuracy. Similarly, spikes of the original MDISE samples were recovered at 125% and 135% by graphite furnace. Dilution spikes showed 95% recovery. However, again a positive interference was not confirmed since good correlation existed between original and dilution analyses. Graphite furnace analyses of SIC 4911 samples followed the same pattern. In all SIC Codes a total of 26 of 36 original sample spikes were recovered in the good or fair range with another six in the poor range. Spiked and original analyses were performed on separate sample aliquots digested on different days. Spikes of the solubilized iron in the sample digest yielded 16 of 18 recoveries in the good or fair range. Since good correlation existed between original and diluted samples these results confirm that variable recoveries were largely due to digestion efficiencies of particulate iron or non-homogeneous sample aliquotting.

The APDC/MIBK chelation/extraction procedure yielded good or fair recoveries for 24 of 36 spikes, poor recoveries for seven of the remaining 11 and recoveries <55% or >145% in five cases. Again, apparent positive or negative interferences could not be confirmed by diluted digest correlation to the original sample result. Similar results were obtained for the PDCA/$CHCl_3$ method.

The VAD often produced results 10% - 40% higher than the MAD particularly for samples from SIC 4911. Sample 4911 016 01 contained a 10X higher iron concentration by VAD than MAD. These results confirm that the efficiency of the digestion impacted observed recoveries. In the latter case where VAD yielded 10X more iron than MAD a non-representative "chunk" of particulate iron may have been aliquotted and digested. This result represents a severe example of problems inherent in withdrawing a representative aliquot from a sample containing high particulate metals.

Precisions for direct aspiration of $\pm$6.0% and $\pm$2.1% were achieved for total iron at concentrations of 0.08 and 2 mg/l.

Good recoveries were achieved for these samples by direct aspiration. A filtered sample was digested and a precision of ±1.3% was achieved by flame. This sample represents precision independent of particulate aliquotting and digestion. Graphite furnace precisions of ±29.4% and ±10.5% were obtained on samples of 18 and 63 ug/l. APDC/MIBK precision was ±18.9% at 115 ug/l while PDCA/$CHCl_3$ was ±8.5% at 90 ug/l.

Dissolved Iron

Samples from SIC 3312 and 3315 were analyzed for dissolved iron. Good recoveries were achieved for all 56 spikes analyzed by direct aspiration.

A negative interference was encountered in SIC 3312 sites 005 and 009 for furnace analyses. Original sample spike recoveries were <50% while diluted spikes were in the good range. A negative interference was also present in one of two SIC 3315 samples. The interference noted by low recoveries was confirmed by the unspiked diluted analysis yielding higher results than the original analysis.

PDCA/$CHCl_3$ chelation/extraction yielded good spike recoveries in 9 of 10 cases with one fair recovery, thus no interferences were identified. A positive interference affected the APDC/MIBK analysis of the site 004 sample of SIC 3315. An original spike recovery of 164% was reduced to 114% for the diluted digest spike.

Mercury

Samples for SIC 1099 and 2812 were analyzed for mercury by the cold vapor technique. Good recoveries were achieved for seven of 12 spikes in SIC 1099 with three of the remaining five recovered in the fair range. One diluted digest sample was recovered to 145% with another at 150%. These two high recoveries appeared to be due to random error rather than interferences since the corresponding original sample spike was recovered nearly to 100%.

Samples from sites 001, 002, and 004 in SIC Code 2812 showed good or fair recoveries, thus, no significant interferences were noted. Samples from sites 006, 008, and 009 showed original sample spike recoveries of only 30% while the diluted digest spikes were recovered between 125% and 175%. Diluted analyses were roughly 25% higher than original analyses indicating the possibility of a small negative interference, but not to the magnitude indicated based on spike recoveries. Random error, drift in standard curve, and possible mercury loss between original digestion and spiked original digestion may magnify the apparent negative interference effects.

Precision of ±7.6% and ±5.6% was achieved on samples containing 6.6 and 10.7 mg/l.

Manganese

No interferences were identified for direct aspiration, furnace, or PDCA/$CHCl_3$ chelation/extraction for the three industrial categories studied. Direct aspiration produced 62 of 68 good recoveries, two fair recoveries, and four poor recoveries. The furnace procedure yielded nine of 14 good recoveries, four fair and two poor recoveries. PDCA/$CHCl_3$ showed good recoveries for 11 of 14 spikes, fair recoveries for two spikes and poor recoveries for one spike.

A standard curve for manganese could not be achieved by the APDC/MIBK chelation/extraction procedure. The EPA methods manual(4) states that the manganese APDC complex breaks quickly and samples should be analyzed as soon as possible once chelated. Approximately one hour passed from time of chelation to time of aspiration. No absorption resulted for standards or samples from the same digests as those used for PDCA/$CHCl_3$. Numerous attempts were made to produce a standard curve without success. Even when standards were aspirated within 30 minutes of chelation no absorption resulted.

The VAD produced up to 27% higher results than the MAD, however, most results agreed to within ±10% or less.

Precisions for direct aspiration were ±3.3%, ±2.4%, and ±1.1% for samples at 1.1, 1.1, and 2.0 mg/l. Precisions of ±8.5% and ±2.9% were achieved for furnace analysis of samples at 100 and 159 ug/l. PDCA/$CHCl_3$ precision was ±58.5% at 60.9 mg/l. The poor precision obtained on this single sample was not indicative of that obtained in duplicate analyses during the course of the project.

Total Nickel

Flame conditions were extremely critical for nickel determinations by direct aspiration. Recoveries of 170% were noted with a slightly rich flame during the analysis of quality control samples. This effect was eliminated when the flame was adjusted to a leaner burn. It is apparent that an oxidizing flame must be maintained for nickel. Since standards and samples are run under the same flame conditions, this source of error should be minimal. However, acid type and concentration may become increasingly important when using a richer flame, and slight variations between samples and standards may cause inaccuracies.

No interferences were detected with direct aspiration or chelation/extraction techniques in the four industrial categories

studied. A spike recovery of only 26% was achieved for one sample analyzed by PDCA/$CHCl_3$. However, this recovery was affected by an apparently erroneous result for one duplicate original analysis. Flame analyses produced 70 of 72 good spike recoveries with the remaining two recovered in the fair range.

A small positive interference was detected in MDISE samples analyzed by graphite furnace. Recoveries of 130% were achieved for original sample spikes while recoveries of 87% and 103% were achieved for spiked 1:2 digest dilutions. The positive interference was confirmed by the 30% - 40% decrease in the dilution analysis. A negative interference was noted in one SIC 2819 sample. Despite these interferences, furnace analyses produced good results with 14 of 18 spikes recovered in the good range.

The VAD produced essentially equivalent results as MAD. Poor correlation ratios for SIC 1099 and MDISE were due to the samples near detection limits.

Precisions of $\pm$1.2% were achieved for direct aspiration and 10% - 11% for graphite furnace. APDC/MIBK and PDCA/$CHCl_3$ produced precisions of $\pm$5.2% and $\pm$1.0%, respectively.

Dissolved Nickel

Samples from SIC 3312 and 3315 were analyzed for dissolved nickel. Direct aspiration produced 55 of 56 spike recoveries in the good range with the remaining one in the fair range. Good results were also generally achieved for the chelation/extraction procedures with 15 of 20 good recoveries, four fair recoveries, and only one poor recovery. The poor recovery (56%) was obtained on one SIC 3315 sample by APDC/MIBK indicating a negative interference.

Seven of 10 recoveries were in the good range for the graphite furnace method with two others in the fair range. A negative interference in one SIC 3312 sample was responsible for one poor recovery (52%). The diluted digest spike was recovered to 74%.

Lead

All 144 spikes in seven industrial categories were recovered in the good range. For SIC 1061, 1099, 2812, 3229, 3312, 3332, and MDISE, the furnace procedure showed 22 of 28 good recoveries and four fair recoveries; the PDCA/$CHCl_3$ method showed 24 of 28 good recoveries; and the APDC/MIBK method produced 21 of 28 good recoveries and three fair recoveries.

SIC 1099 contained a negative matrix interference affecting both chelation/extraction procedures and the furnace procedure.

PDCA/$CHCl_3$ produced recoveries of 62% and 80% for original sample spikes, and 103% and 84% for diluted digest spikes. The APDC/MIBK method yielded 54% recoveries for original sample spikes and 91% - 97% recoveries for diluted digest spikes. The furnace procedure was more severely affected showing recoveries no higher than 28%.

A small positive interference affected the APDC/MIBK results for SIC 2812. Original recoveries of about 130% were achieved in both SIC 2812 samples, whereas diluted recoveries were nearly 100%.

Considering that samples only marginally above the detection limit of 100 ug/l were available for VAD to MAD comparisons, similar results were obtained. Two samples at 1400 and 600 ug/l agreed exactly. Quality control samples compared to within ±2% at concentrations of 10 mg/l.

Direct aspiration precisions of ±1.2%, ±3.5%, and ±0.8% were achieved for samples spiked to 5, 10, and 15 ug/l. Furnace precisions of ±181% and ±10.3% were achieved for samples at 9 ug/l and 34 ug/l. An interference was responsible for poor precision on the former sample as it was spiked to 20 ug/l and results varied from <1 ug/l to 45 ug/l for an average of 8.9 ug/l. A 500 ug/l sample yielded precision of ±6.6% for APDC/MIBK and ±5.0% for PDCA/$CHCl_3$.

Tin

Good results were obtained for tin determinations by direct aspiration as 62 of 64 spikes were recovered in the good range for the three industrial effluents studied, SIC 3312, 3471, and MDISE. The other two recoveries were in the fair range.

However, little tin was recovered in graphite furnace analyses. Even quality control samples produced low recoveries for furnace analyses. These low recoveries were not due to the analytical detection technique, but rather were due to the digestion technique utilized prior to analysis. The MAD was employed for both flame and furnace techniques, however, hydrochloric acid was used with nitric acid for flame analyses while only nitric acid was used in the furnace technique for MDISE. After low recoveries were noted hydrochloric acid was added to prevent tin precipitation for SIC 3312 and 3471. Hydrochloric acid was maintained at 2% in an attempt to keep tin in solution without causing significant furnace interferences. However, at low level furnace concentrations tin was still lost even with HCl.

MDISE and SIC 3471 samples analyzed for VAD/MAD comparisons were below detectable levels. Good correlation (±8%) was achieved for a 7 mg/l sample in SIC 3312.

Precisions of ±12.5%, ±15.4%, and ±0.8% were achieved for direct aspiration. Furnace precisions were ±36.2% and ±14.5% for samples at 20 and 78 ug/l. It should be noted that the 20 ug/l sample was spiked to 100 ug/l, thus, again poor tin recovery was achieved.

Zinc

The direct aspiration technique for zinc proved to be quite successful in the 10 industrial categories studied. Only eight of 172 spikes were recovered outside of the fair range with 147 of 172 recovered in the good range. Good dilution correlation was also achieved. Only the two samples from site 010 of SIC 3312 exhibited a positive interference as evidenced by recoveries of 160%.

Serious problems affected graphite furnace determinations. Zinc is the most sensitive element by the atomic absorption technique. Contamination in this extremely sensitive technique is the major problem. Analyses of MDISE and SIC 3331 samples were performed utilizing the Perkin-Elmer Model 500 Graphite Furnace and the Model 5000 Atomic Absorption Spectrophotometer. Contamination was so severe during both manual and auto-injection that essentially meaningless data were generated. For all other samples in SIC 1061, 1094, 2621, 2823, 3312, 3332, 3333, and 3341 the Perkin-Elmer HGA 2100 furnace was used in conjunction with the Perkin-Elmer Model 370 AAS. The HGA 2100 was 2 - 3X less sensitive than the 500 furnace and contamination from manual injection was therefore relatively less severe. For the latter SIC Codes, 19 of 36 spikes were recovered in the good range, 11 of the remaining 15 were recovered in the fair range, and an additional three in the poor range. Thus, by utilizing a less sensitive furnace, contamination effects during injection were minimized and more reasonable results were achieved. The purpose of using furnace to achieve greater sensitivity was, however, partially defeated by using a less sensitive instrument. Injection into the furnace must be carefully controlled. The slightest contact of the pipette tip with the exterior of the graphite tube added gross contamination. Auto-injection produced even greater contamination than manual injection.

The chelation/extraction procedures produced occasional high spike recoveries (as much as 200%) for quality control samples, an indication of contamination. Sources of contamination from glassware and reagents were increased for the 3-step digestion/extraction/detection procedures over the 2-step direct aspiration and furnace procedures. The PDCA/$CHCl_3$ procedure produced 10 of 38 good spike recoveries, an additional eight fair recoveries, and another six poor recoveries. Twelve spikes were recovered below 55%. The APDC/MIBK method produced somewhat better results for zinc than the PDCA/$CHCl_3$ with 18 of 42 spikes recovered in

the good range, an additional 10 in the fair range, six in the fair range, and five below 55%. Interferences were difficult to identify since contamination caused high or low recoveries depending on whether it was greater in the unspiked or spiked analyses.

Thus, for furnace and chelation/extraction methods contamination present in glassware, reagents, and instrumentation was the greatest limitation to successful zinc determinations. Zinc is a common element in the laboratory, and contamination effects are magnified by the furnace and chelation/extraction methods due to their greater sensitivities and more complex sample preparation or instrumental detection systems.

The VAD produced lower results than MAD for SIC 1094 samples 5X to 10X above the 5 ug/l detection limit. Good correlation was achieved for other samples.

Precisions of $\pm$4.8%, $\pm$2.1%, and $\pm$0.8% were achieved for direct aspiration at sample concentrations of 77, 630, 2000 ug/l. Poor furnace precisions of $\pm$93.3% and $\pm$174% were achieved. Chelation/extraction precision of $\pm$6.3% and $\pm$19.7% was achieved for a 35 ug/l sample by APDC/MIBK and PDCA/$CHCl_3$.

Arsenic

The graphite furnace technique for arsenic produced good recoveries for 75 of 108 spikes. Three samples collected from site 001 in SIC 3333 had a definite positive interference. Recoveries of 130% - 160% were achieved for the spiked original and diluted digests. The diluted digest spike recoveries were approximately equal to or less than the recovery of the original spike. Severe negative interferences were encountered in site 001, 002, 006 and 008 of SIC 2819 resulting in essentially 0% recoveries for original spiked samples and marginally higher recoveries for diluted digest spikes.

The sodium borohydride hydride generation method produced good or fair recoveries for SIC 1061, 3331, 3333, and MDISE samples with one exception in SIC 3333 where one member of a spiked duplicate pair exhibited a recovery of 10% with the other member showing an 80% recovery. This discrepancy appeared to be an isolated occurance. Four of six samples in SIC 1094 exhibited positive interferences resulting in 180% to 220% recoveries. Five of nine samples in SIC 2819 were affected by negative interferences showing recoveries between 0% and 40%. One SIC 2819 sample exhibited a positive interference as noted by a 500% recovery.

The zinc slurry method of hydride generation yielded relatively poor results. Most (40 of 54) original spikes were

recovered to 55% or less. However, 28 of 54 diluted digest spikes were recovered in the good range with 16 of the remaining 26 recovered in the fair range, and only four recovered below 55% (all in SIC 2819). Thus, the digestion appeared to be the source of arsenic loss. This method is also limited by poor standard curve linearity and precision, as well as arsenic contamination in some lots of zinc powder.

Good precision was achieved for graphite furnace determinations, ±4.7% and ±2.4% for 34 and 54 ug/l. Zinc slurry hydride generation precisions were ±17.7% and ±6.7% for concentrations of 14 and 18 ug/l.

Selenium

The graphite furnace technique for selenium proved quite successful for SIC 3331, 3333, and MDISE with only three of 36 spikes recovered outside of the fair or good ranges. Sixteen of 18 diluted digests correlated with the original determination within ±30%. The arsenic interference present in SIC 3333 had no effect on selenium determinations. However, similar negative interferences as encountered with arsenic affected SIC 2819 determinations. Varying degrees of negative interferences were present in site 001, 002, 004, 005, 006, 007, and 008 of SIC 2819.

The sodium borohydride hydride generation method yielded good or fair recoveries with no apparent interferences for SIC 3331, 3333, and MDISE. Again as with arsenic negative interferences affected SIC 2819 results in sites 001, 004, 006, 007, and 008.

The zinc slurry hydride generation method for selenium proved even less effective than for arsenic. Selenium was also apparently lost in the digestion. However, poor recoveries were achieved even for spikes of previously digested sample aliquots. Poor standard curve precision and linearity greatly limited the accuracy of data calculations.

Graphite furnace precisions of ±20.8% and ±5.8% were achieved for samples at 5 and 23 ug/l. Zinc slurry hydride generation precision was ±0% and ±39% for determined concentrations of 2 and 4 ug/l. Samples were spiked at 10 ug/l for the zinc slurry method, thus, loss of selenium was evident during digestion.

General

Trace metal methods correlation tables are provided in Appendix III. Results for samples analyzed by more than one AAS method are listed in columns by technique. In evaluating these

data for method equivalency several factors should be considered including a) method precision, b) analytical value with respect to analytical range and detection limit, c) presence or absence of matrix interferences, and d) other method limitations such as sources of contamination.

Samples from SIC 2819 caused interferences for most metals and techniques. Interferences in sites 006 and 008 were particularly severe. These sites contained high levels of organic materials as noted by the presence of sludge (site 006) or high viscosity (site 008). All SIC 2819 samples were also high in dissolved salts.

CYANIDES

Samples were analyzed for total cyanide from eight industrial categories. Raw data tables with all duplicate determinations and calculated mean, range, spike recovery, and sample concentrations are presented in Appendix II. Manipulated data appears in Appendix I showing the following relationsihps:

- o Spike recoveries by SIC Code (Table 116)
- o Comparison of diluted versus concentrated sample analyses (Table 117)
- o Evaluation of method equivalency (Tables 118)
- o Preservation studies (Tables 120)
- o Precision studies (Tables 119)

Analytical results are described below.

Pyridine Barbituric Acid Colorimetric Method (PBA)

The pyridine barbituric acid method (PBA) was utilized for all distillations containing <1 mg/l cyanide. Over the eight industrial categories 89 of 164 spikes were recovered in the good range, an additional 47 spikes were recovered in the fair range, and eight in the poor range. Low recoveries of <55% were obtained for 18 spikes and two were recovered over 145%. Quality control samples were generally recovered between 85% and 100% indicating a slight loss in the distillation step.

Samples from SIC 1099 and 3471 showed no PBA interferences as all spikes were recovered in the good range. Good or fair recoveries were achieved for 22 of 24 spikes for MDISE and SIC

3861 with the remaining two spikes only marginally lower. Most spikes were recovered in the 70% - 100% range rather than 100% - 130%, probably a function of the distillation efficiency. Spike recoveries were marginally lower for SIC 3861 samples than for simultaneously run quality control samples, however, no significant negative interferences were apparent. Diluted sample analyses correlated to within ±15% of the original analyses for 11 of 12 MDISE and SIC 3861 data points.

Severe to moderate negative interferences affecting the PBA method were present in 10 of 62 samples from SIC 2819, 3312, 3313, and 3315. Samples from sites 002 and 006 of SIC 2819 exhibited no spike recovery. Site 006 contained a black organic and inorganic sludge with an ammonia odor. Site 002 samples displayed no visual peculiarities. Sample 2 from site 009 in SIC 2819 varied markedly in PBA response. Several distillates had low absorbances while others were off-scale in absorbance readings. Apparently an interference distilled over to varying degrees. The rate of distillation was probably the factor determining interference concentration in the distillate. Some distillates from this sample formed a red precipitate with reagent addition.

Both site 003 samples and sample 2 of site 007 in SIC 3312 exhibited negative interferences as noted by recoveries in the 14% - 55% range. Sample 3313 005 2 exhibited a negative interference as observed from a 9% original sample spike recovery and a 47% diluted sample recovery. A 268% recovery was achieved for sample 2 of site 003 in SIC 3313, however, this recovery appears to be random error as one of the duplicates was excessively high. Site 003 sample 1 in SIC 3315 showed a moderate negative interference. All sample distillates were checked for the sulfide interference, but none was found for PBA samples.

Good or fair recoveries were generally achieved for the remaining 72 samples analyzed by the PBA colorimetric method.

Silver Nitrate Titrimetric Method

Four samples containing greater than 1 mg/l cyanide were analyzed by the titrimetric method (TTM). One good and one fair recovery was achieved for the SIC 3471 sample, and no interferences were noted.

Three samples were analyzed in SIC 3312 by the titrimetric method. The two samples from site 001 contained high levels of sulfide in the distillate, and cadmium carbonate was used to eliminate this known interference. Spike recoveries of 112% and 157% were achieved for one of these samples with only 47% and 0% recovered for the other. However, the 1 mg/l spike accounted for only 10% - 20% of the total cyanide in this sample. Good recoveries were achieved for the third SIC 3312 sample.

Colorimetric Methods Comparison

Diluted spiked samples with cyanide below 1 mg/l were analyzed by both the PBA and the PPC colorimetric methods. Analyses were conducted on common distillates. Results are presented in Appendix I. The methods produced equivalent results in all cases with the largest variation in 82 comparable analyses being only 20%. Interferences affected both procedures similarly.

Method Precision

Precision for the titrimetric and colorimetric methods was determined by analyzing seven replicates put through the entire analytical procedure including digestion. Precision for the colorimetric methods was determined on common distillates. Precision replicates are presented in Appendix I and the data is compiled in Table 21.

TABLE 21. PRECISION DATA, CYANIDES

SIC Code	PBA			PPC			TTM		
	x	s	cv	x	s	cv	x	s	cv
2819	279.9	±9.4	(3.4%)	272.4	±11.9	(4.4%)	----------		
	45.0	±1.0	(2.2%)	45.3	±2.1	(4.6%)	----------		
3312	161.7	±3.3	(2.0%)	161.4	±3.5	(2.2%)	----------		
	----------			----------			1295	±78	(6.0%)
3313	241.7	±6.5	(2.7%)	251.4	±4.1	(1.6%)	----------		
	39.3	±2.5	(6.4%)	38.0	±1.9	(5.0%)	----------		
3315	47.0	±5.3	(11.3%)	46.9	±5.3	(11.3%)	----------		
	69.4	±1.3	(1.9%)	67.1	±1.3	(1.9%)	----------		
3861	40.7	±3.4	(8.4%)	39.0	±2.1	(5.4%)	----------		
	279.6	±9.2	(3.3%)	231.7	±7.9	(3.4%)			

Preservation Studies

One 10-day preservation study was performed for each of five industrial classifications. Three of the samples collected for these studies (SIC 1099, 3313, 3315) were found to contain low level cyanide concentrations near the detection limit, thus

cyanide loss was difficult to monitor. Samples from SIC 3861 and SIC 3312 contained approximately 80 ug/l and 30 ug/l, respectively. No significant cyanide loss occurred for these samples over the 10-day preservation period as seen in Figures 4 and 5. Samples were preserved with sodium hydroxide to a pH >12 and kept refrigerated at 4°C.

PHENOLICS

Raw data tables for phenolics are presented in Appendix II and manipulated data is presented in Appendix I as follows:

- Spike recovery distribution (Table 111)
- Diluted versus concentrated sample analysis correlation (Table 112)
- Methods comparison (Table 113)
- Precision studies (Tables 114)
- Preservation studies (Tables 115)

Results for these studies are discussed below.

4-AAP Colorimetric Method

Good spike recoveries by the 4-AAP method were achieved in 112 of 256 determinations and fair recoveries were achieved in 74 determinations in 10 industrial categories. Only 35 recoveries were <55% or >145%. Occasionally a diluted sample exhibited significantly lower or higher recoveries than the corresponding original concentrated analysis indicating an interference not noted in the original sample. This phenomenan could indicate that the distillation of interferences was not always consistent. The rate of distillation, homogeneity of interfering substances in the sample and other factors could impact on the level of interferences in any distillate. Varying degrees of interferences between distillates would not be seen within duplicate pairs because the duplicates were run on common distillates. These effects would impact recoveries since spikes were made prior to distillation.

A negative interference affected recoveries in two of 12 SIC 2231 samples. Sample 1 from site 005 showed no recovery for the original sample spike and a 25% recovery for the spiked dilution. The diluted sample was determined to contain twice the original sample analysis (342 ug/l compared to 198 ug/l), thus, the negative interference was confirmed. Sample 2 from site 006 also

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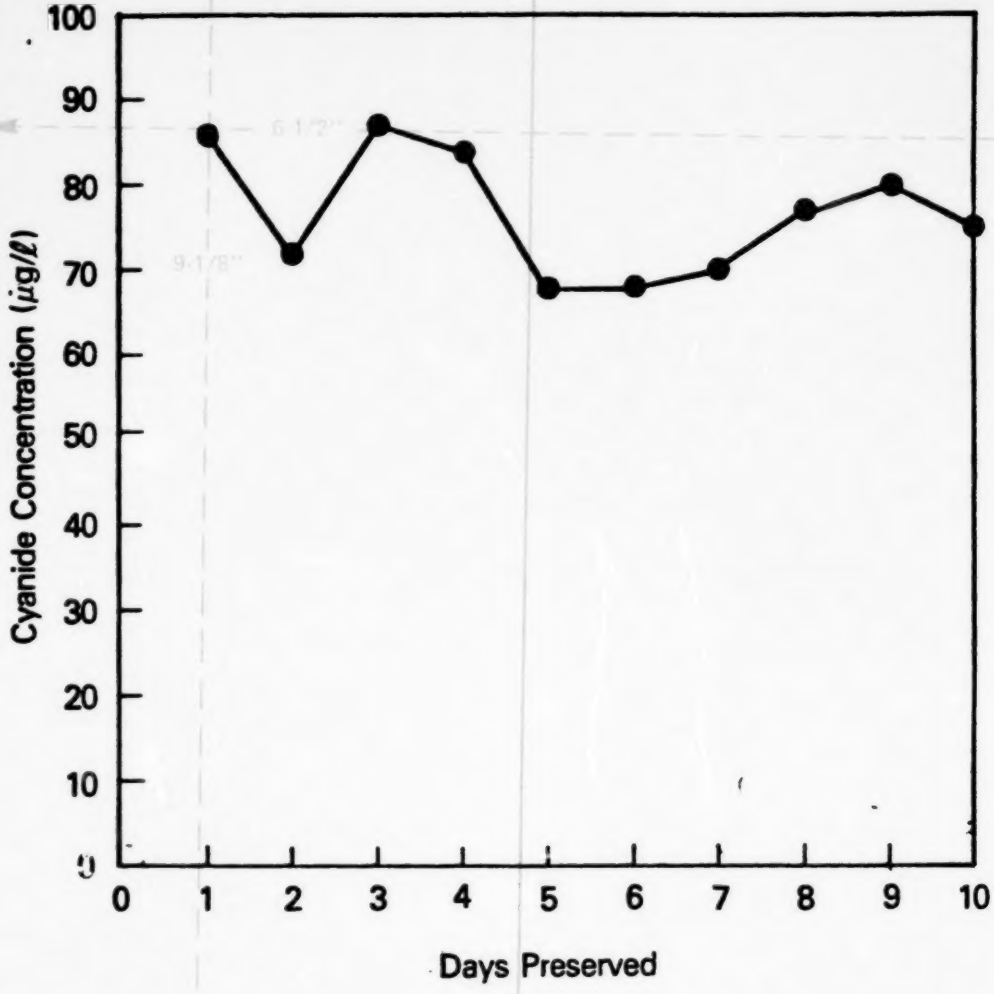
Figure 4

Cyanide Preservation Study

Sample 3861 003 7



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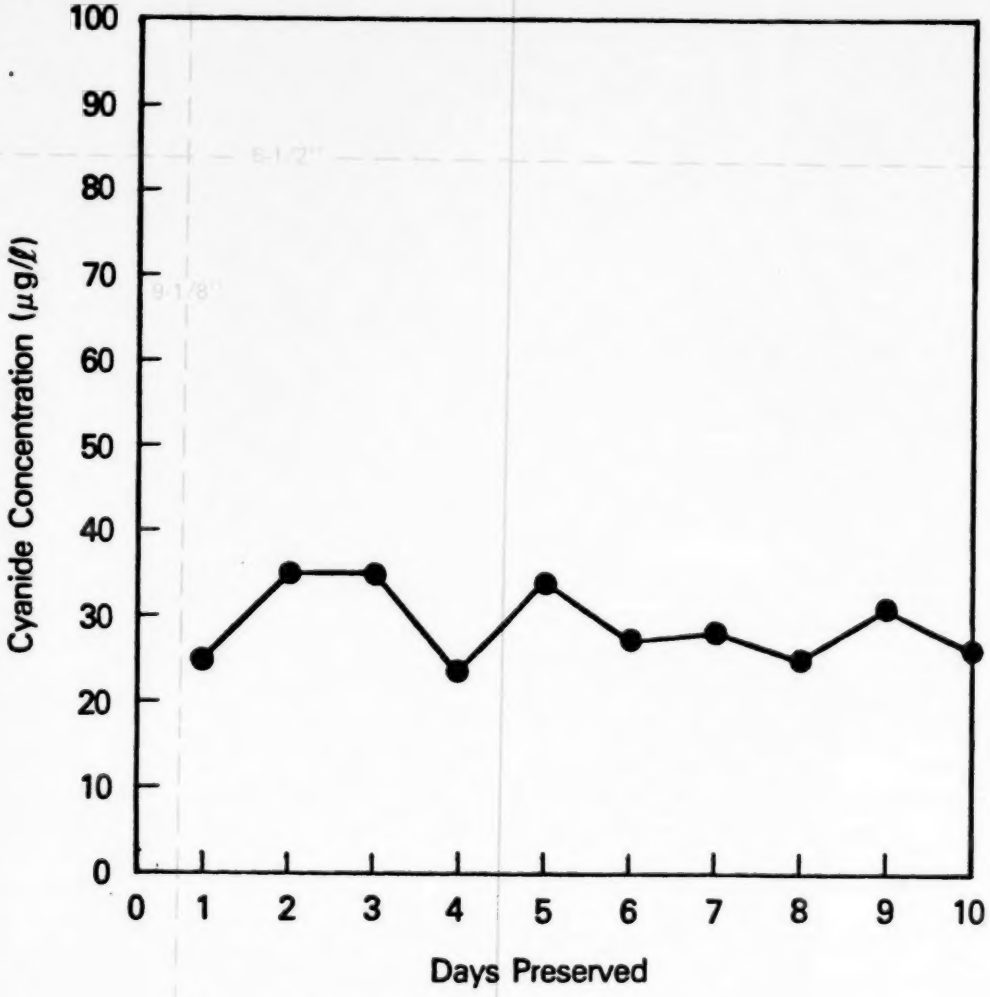
TYPING GUIDE SHEET

Figure 5

Cyanide Preservation Study

Sample 3312 010 7



contained a negative interference showing a 16% original sample spike recovery and 61% dilution spike recovery. Again the interference was confirmed by the dilution reading 35% higher than the original analysis. The other 10 samples in SIC 2231 showed good to fair recoveries.

Four samples from sites 005 and 006 in SIC 2262 exhibited positive interferences with spikes recovered between 150% and 250%. Generally good or fair recoveries were achieved for the other eight samples of sites 001-004.

Good recoveries were achieved in 13 of 16 spikes for SIC 2491 samples with the other three recovered in the fair range. No interferences were identified in this SIC Code.

SIC 2821 samples exhibited poorer results than most other SIC Codes with only seven of 28 good recoveries and 10 fair recoveries. Interferences were not as severe as in other SIC Codes, but a larger percentage of samples were affected. Moderate negative interferences were identified in six samples from sites 004, 006, and 007 of SIC 2821, where recoveries of 45% -75% were achieved.

A moderate negative interference affected sample 1 in site 003 of SIC 2879 resulting in 46% - 65% recoveries. Recoveries appeared poor for samples in site 001, however, these samples contained high levels of phenolics and the resultant spikes accounted for only a small percentage of the total. With these exceptions, generally good or fair results were achieved for the remaining samples.

A severe negative interference in SIC 3312 was identified in site 009 sample 2 where essentially 0% recoveries were achieved. A more moderate negative interference affected sample 1 in site 009 and samples in site 010. Negative interferences also affected results in SIC 3313 for four samples in sites 002 and 006.

Samples from SIC 2911, 3861, and MDISE generally showed good or fair recoveries with 41 of 80 spikes recovered in the good range, 21 in the fair range, and only three below 55%.

PH-3 Instrumental Method (PHI)

The PH-3 instrumental (PHI) method was evaluated using the same distillates as the 4-AAP method. Spikes were added to the samples based on the original concentrations as determined by 4-AAP. A large discrepancy often existed between 4-AAP and instrumental results (PHI yielded much higher values), thus, the spikes in many cases represented only small percentages of the phenolics detected by the instrument, and were an insignificant

addition relative to precision. This factor must be considered when evaluating spike recoveries which were <55% or >145% for 171 of 256 determinations. However, the overriding factor for poor recoveries appeared to be method related rather than spike related. Duplicate analyses performed on common distillates usually yielded precise results. However, precision between separate distillates was suspect, as evidenced by significantly higher or lower results obtained for spiked samples than for unspiked samples. In cases where the spikes were insignificant compared to total phenol concentration, results should have been similar for spiked and unspiked samples, but reproducibility between distillates was not achieved.

High background levels were partially responsible for the lack of reproducible results between distillates. In many cases, the background levels contributed 50% - 80% of the total signal. Detection limits were often sacrificed by the necessity of using smaller path length cells or dilutions to reduce background levels to achieve on-scale responses. In compensating for the background, a large potential error was introduced. The background level was not reproducible between distillates, thus, the degree of error in compensating for the background signal varied for each distillate. The rate of distillation may be a determining factor for background levels.

Distillation as a means of sample preparation is unacceptable for instrumental detection. An alternate sample preparation step such as solvent extraction followed by a back extraction into water may produce better results.

MBTH Colorimetric Method

Separate samples preserved in sulfuric acid were distilled and analyzed by the MBTH colorimetric method since phosphoric acid is an interference with MBTH. Spikes were recovered in the good range for 64 of 256 analyses and in the fair range for 48 additional spikes. Seventy-eight spikes were recovered at <55% and 31 at >145%.

As evident from these recoveries significant interferences were encountered in all SIC Codes. Poor recoveries were obtained on samples from SIC 3861 with nine of 12 spikes recovered at levels <55% or >145%. However, all diluted SIC 3861 sample analyses correlated to within 30% of the original analyses. Several samples in SIC 2911 exhibited positive or negative interferences with 13 of 56 spikes recovered <55% or >145%. Severe negative interferences affected samples from site 004 in SIC 2821 where all determinations including spikes gave no absorbance readings thus, 0% recoveries. Additional negative interferences in SIC 2821 although not as severe significantly affected the MBTH determinations in samples from sites 001, 005,

006, and 007. Negative interferences were present in SIC 2231, sites 001 and 002. Severe negative interferences resulted in 0% recoveries for site 006 samples in SIC 2262 and also affected samples in sites 001, 002, and 003. Generally poor results or worse were achieved for SIC 3313 samples with severe negative interferences resulting in 14 of 24 spikes recovered below 55%. Only eight recoveries for this SIC Code were in the good or fair range. Positive interferences were prevalent in SIC 2491 with half of the eight samples affected. Similar positive and negative interferences were encountered in SIC 2879 and 3312. Only MDISE samples were free of interferring matrices.

Two indicators of interferences were observed throughout the study. First, samples often turned cloudy upon addition of reagents causing positive interferences. Second, formation of a deep green or blue color (possibly due to aldehyde reactions) was often formed rather than the normal pink resulting in negative interferences. Another problem associated with the MBTH method was the generation of high zeroes and blanks which were often higher than or near the low level standards. Zeroes could not be subtracted from samples because the presence of even low levels of phenolics nullified the zero response producing standards below zero levels.

Methods Comparison

Sample concentrations as determined by the three methods are presented in Appendix I. MBTH and instrumental results (PHI) are ratioed with the 4-AAP response to show correlation. The methods did not produce equivalent results. The PHI method yielded sample concentrations consistently higher than MBTH and 4-AAP, with MBTH averaging roughly 2X higher than 4-AAP. Samples containing high phenolic concentrations (1 mg/l or more) usually produced fairly equivalent results for the three methods. These samples were diluted to achieve on-scale readings by the colorimetric method, thus, interferences were minimized. It is difficult to assess if the high PHI results were due to interferences or substituted phenolics not reactive with 4-AAP.

Method Precision

Precision for each method was determined from seven replicate analyses put through the entire analytical protocol including distillation. All three procedures were run on common replicate distillates from samples preserved with sulfuric acid. Replicate results are presented in Appendix I and data is compiled in Table 22. Precision varied within SIC Codes probably dependent on interference effects. Precisions were not equivalent for the three methods, partially a function of interference effects specific to each method.

Preservation Studies

Two 10-day preservation studies were performed on each of the nine SIC Codes, one for sulfuric acid preservation and one for phosphoric acid. All analyses were conducted by the 4-AAP colorimetric method. Results are tabulated in Appendix I and are presented graphically in Figures 6-14. No significant loss of phenolics was observed for sulfuric or phosphoric acid preserved samples in SIC 2231, 2491, 2262, 2821, 2911, 3312, or 3313. Some loss over the last 2 - 3 days occurred in samples of SIC 3861. Interferences described earlier caused erratic data in SIC 2879. Small increases in phenolic concentrations occurred with time in some samples perhaps due to changes in phenolic substitution increasing reactivity with 4-AAP.

TABLE 22. PRECISION STUDIES, PHENOLICS

SIC	AAP			MBT			PHI		
	x	s	cv	x	s	cv	x	s	cv
2231	87 ±	17	(19.5%)	67 ±	16	(23.9%)	1,878 ±	1,110	(59.1%)
	76 ±	8	(10.5%)	79 ±	12	(15.2%)	1,223 ±	500	(40.9%)
	625 ±	79	(12.6%)	733 ±	160	(21.8%)	1,275 ±	341	(26.7%)
	161 ±	72	(44.7%)	318 ±	99	(31.1%)	248 ±	111	(44.8%)
	182 ±	72	(39.6%)	238 ±	57	(23.9%)	341 ±	146	(42.8%)
	74 ±	21	(28.4%)	178 ±	52	(29.2%)	620 ±	423	(68.2%)
2821	10,000 ±	136	(1.4%)	8,300 ±	658	(7.9%)	10,080 ±	2,520	(25.0%)
	29 ±	6	(20.7%)	38 ±	11	(28.9%)	92 ±	92	(100/0%)
	781 ±	35	(4.5%)	1,613 ±	68	(4.2%)	1,139 ±	338	(29.7%)
	96 ±	37	(38.5%)	<5 ±	0	(0%)	54 ±	75	(138.9%)
	91 ±	7	(7.7%)	169 ±	80	(47.3%)	601 ±	253	(42.1%)
	93 ±	14	(15.1%)	120 ±	48	(40.0%)	641 ±	239	(37.3%)
2911	129 ±	7	(5.4%)	335 ±	27	(8.1%)	706 ±	98	(13.9%)
	309 ±	16	(5.2%)	284 ±	53	(18.7%)	579 ±	90	(15.5%)
	490 ±	14	(2.9%)	529 ±	21	(4.0%)	1,311 ±	165	(12.6%)
	25 ±	3	(12.0%)	42 ±	4	(9.5%)	576 ±	240	(41.7%)
	25 ±	4	(16.0%)	44 ±	4	(9.1%)	364 ±	179	(49.2%)
	85 ±	5	(5.9%)	103 ±	1	(1.0%)	208 ±	28	(13.5%)
3312	26,800 ±	482	(1.8%)	28,900 ±	2,140	(7.4%)	29,300 ±	4,260	(14.5%)
	32,500 ±	1,135	(3.5%)	34,400 ±	3,040	(8.8%)	36,500 ±	400	(1.1%)
	229 ±	26	(11.4%)	282 ±	70	(24.8%)	748 ±	346	(46.3%)
	127 ±	20	(15.7%)	371 ±	80	(21.6%)	254 ±	94	(37.0%)
	764 ±	76	(9.9%)	669 ±	90	(13.5%)	1,257 ±	422	(33.6%)
	805 ±	360	(44.7%)	742 ±	466	(62.8%)	699 ±	164	(23.5%)
	169 ±	20	(11.8%)	131 ±	48	(36.6%)	667 ±	220	(33.0%)
	166 ±	38	(22.9%)	87 ±	41	(47.1%)	667 ±	220	(33.0%)

TABLE 22. PRECISION STUDIES, PHENOLICS
(continued)

SIC	AAP			MBT			PHI		
	x	s	cv	x	s	cv	x	s	cv
3313	129 ±	19	(14.7%)	229 ±	92	(40.2%)	200 ±	28	(39.0%)
	110 ±	23	(20.9%)	85 ±	8	(9.4%)	153 ±	58	(37.9%)
	450 ±	22	(4.9%)	495 ±	59	(11.9%)	558 ±	113	(20.3%)
	171 ±	32	(18.7%)	58 ±	16	(27.6%)	338 ±	41	(12.1%)
	56 ±	6	(10.7%)	60 ±	6	(10.0%)	234 ±	118	(50.4%)
	58 ±	5	(8.6%)	42 ±	11	(26.2%)	185 ±	172	(93.0%)

Figure 6

Phenolic Preservation Study

Sample 2231 003 7

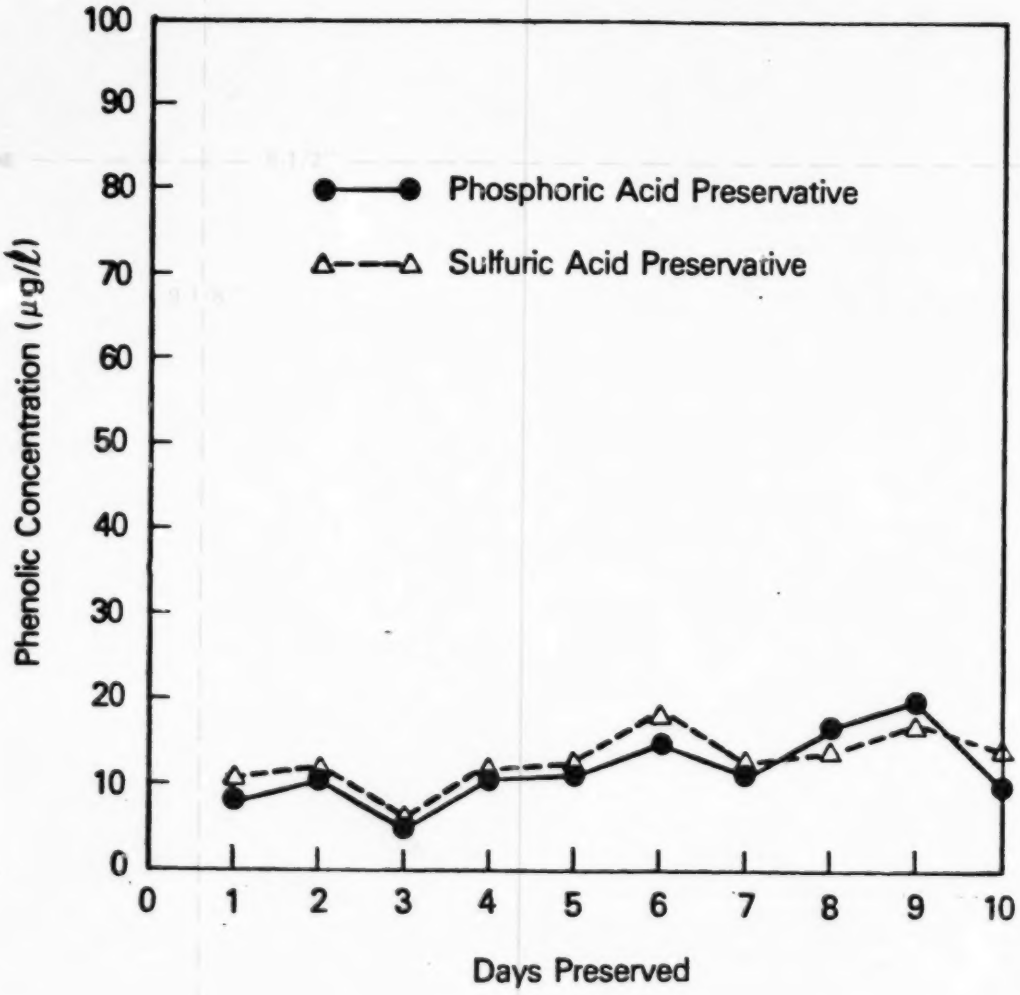


Figure 7

Phenolic Preservation Study

Sample 2262 003 7

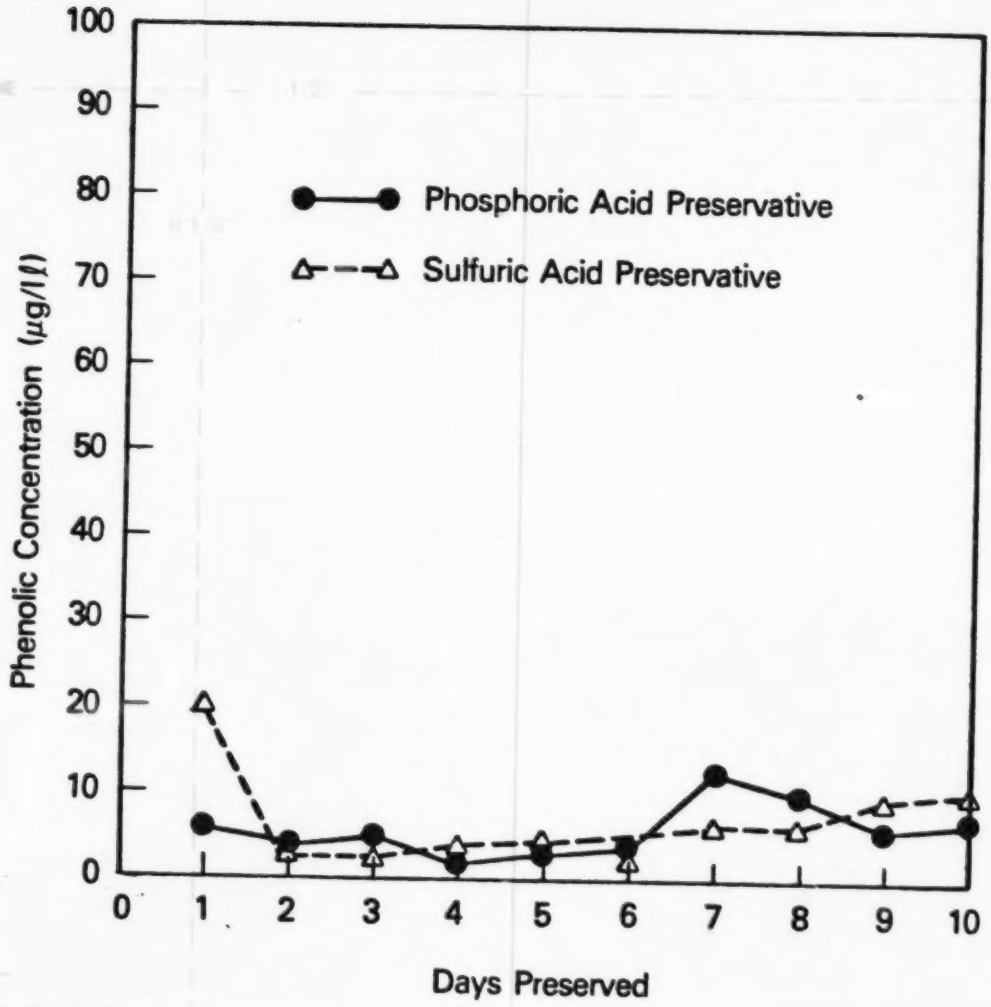


Figure 8

Phenolic Preservation Study

Sample 2491 004 7

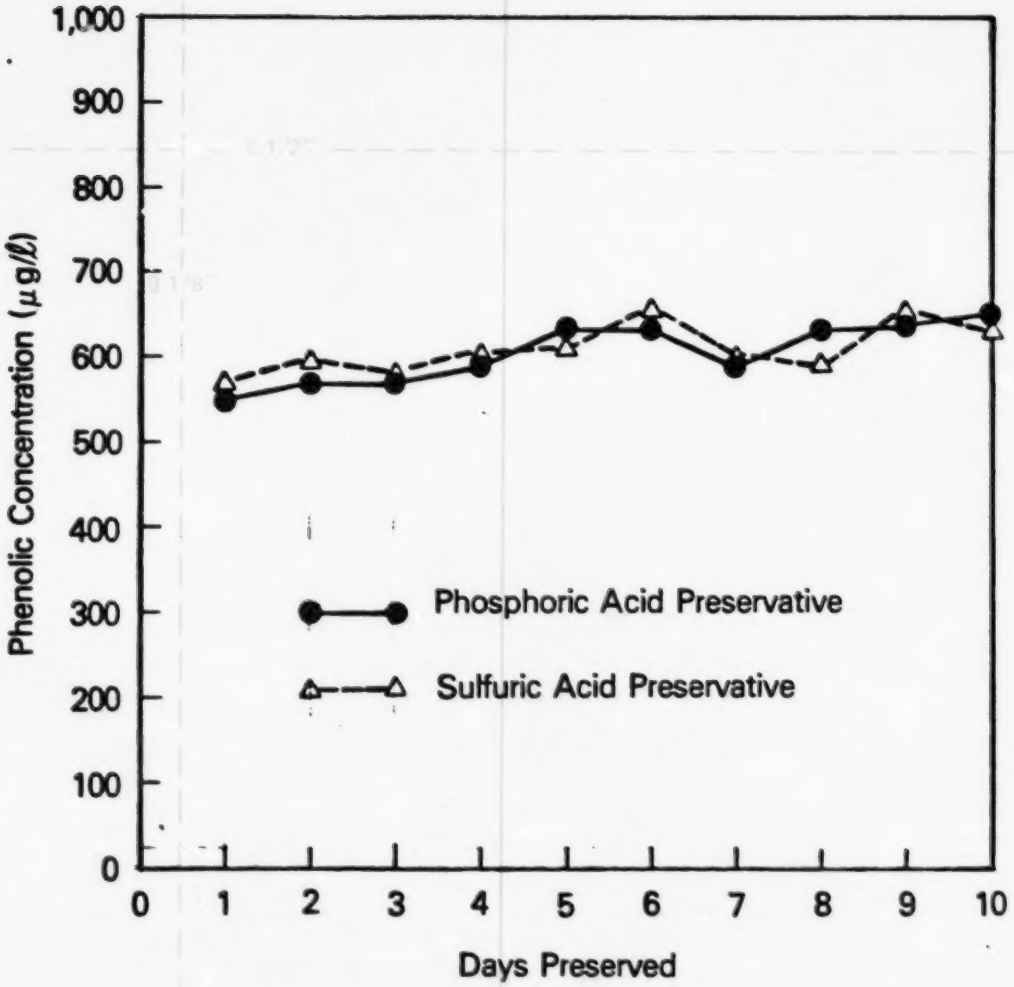


Figure 9

Phenolic Preservation Study

Sample 2821 004 7

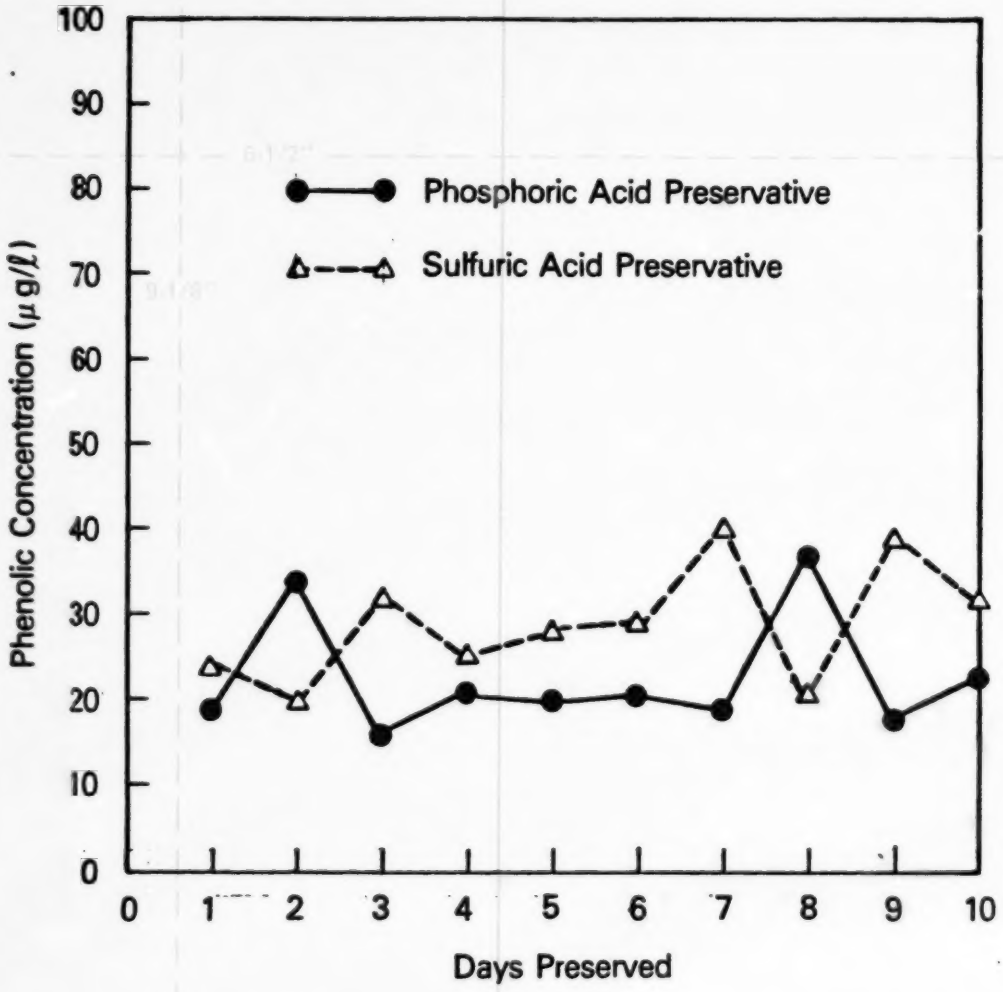
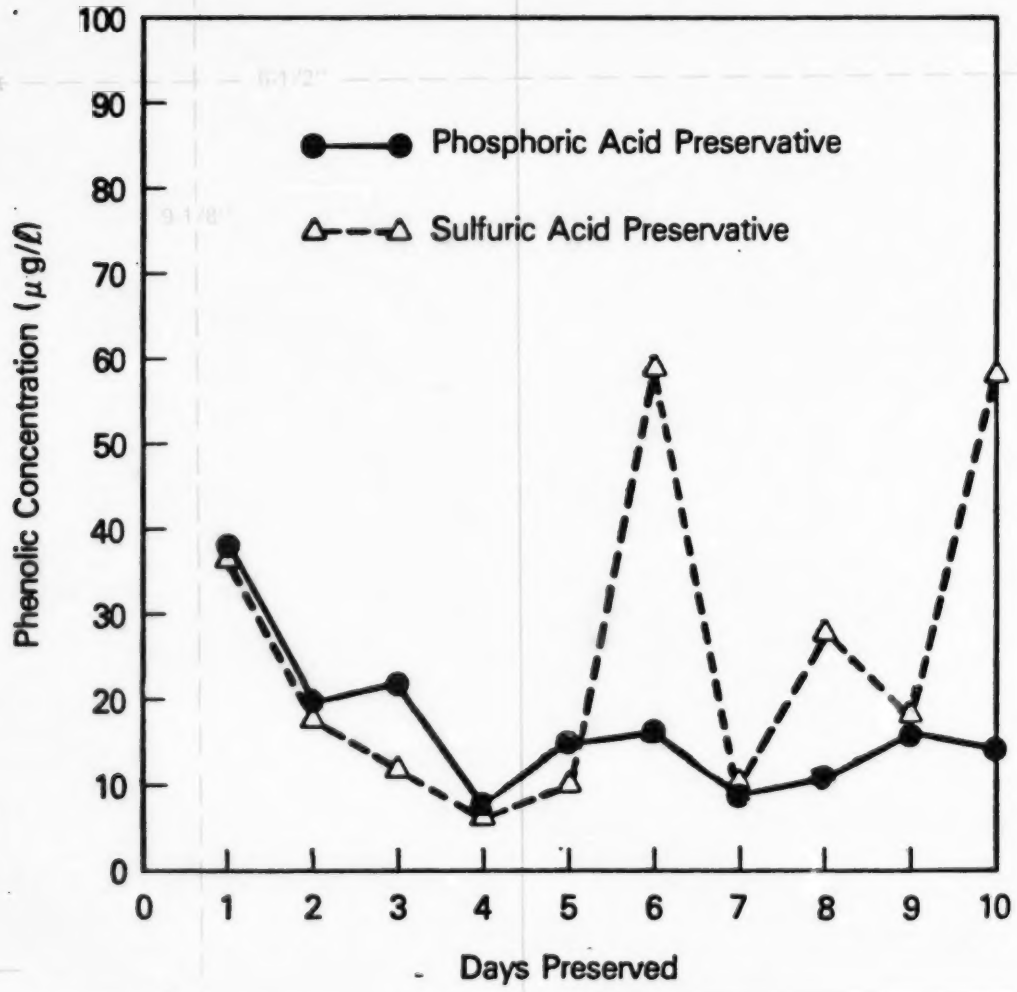


Figure 10

Phenolic Preservation Study

Sample 2879 005 7*



* Interference Present in Sample, see Text.

Figure 11

Phenolic Preservation Study

Sample 2911 004 7

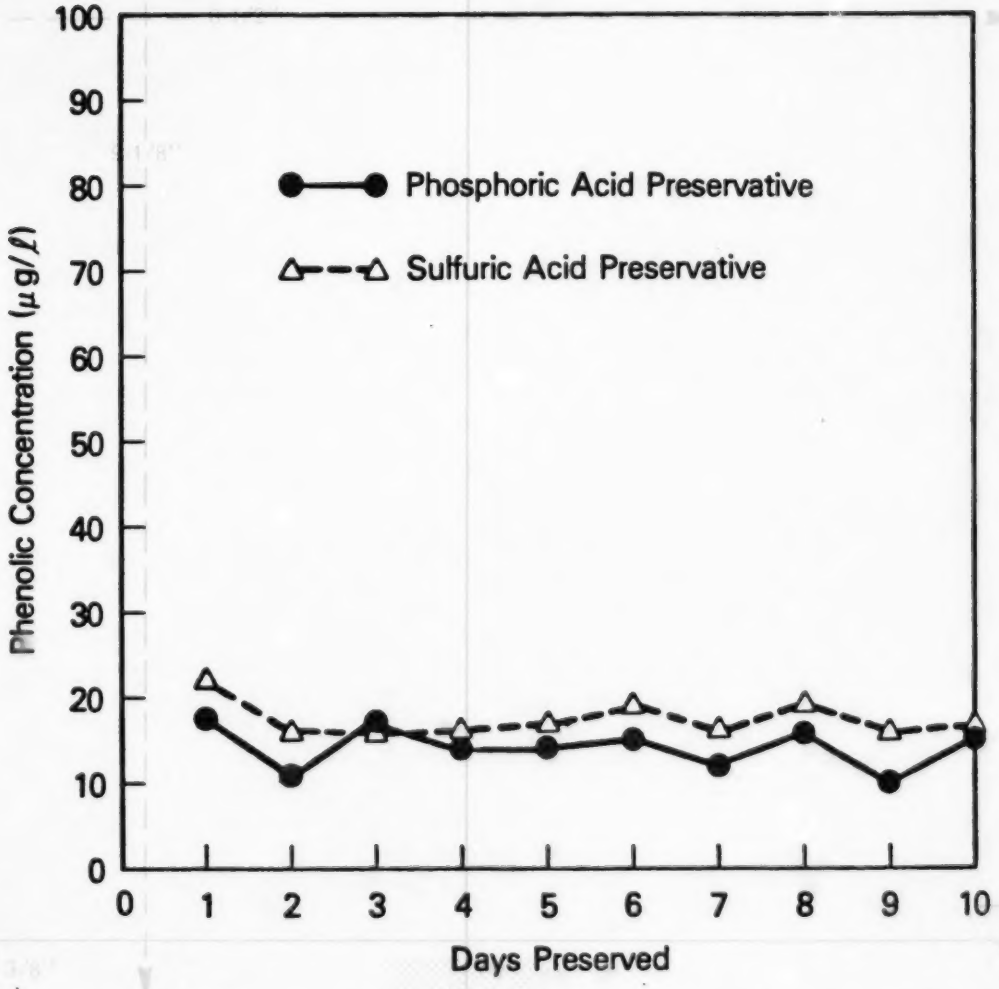


Figure 12.

Preservation Study

Sample 3312 010 7

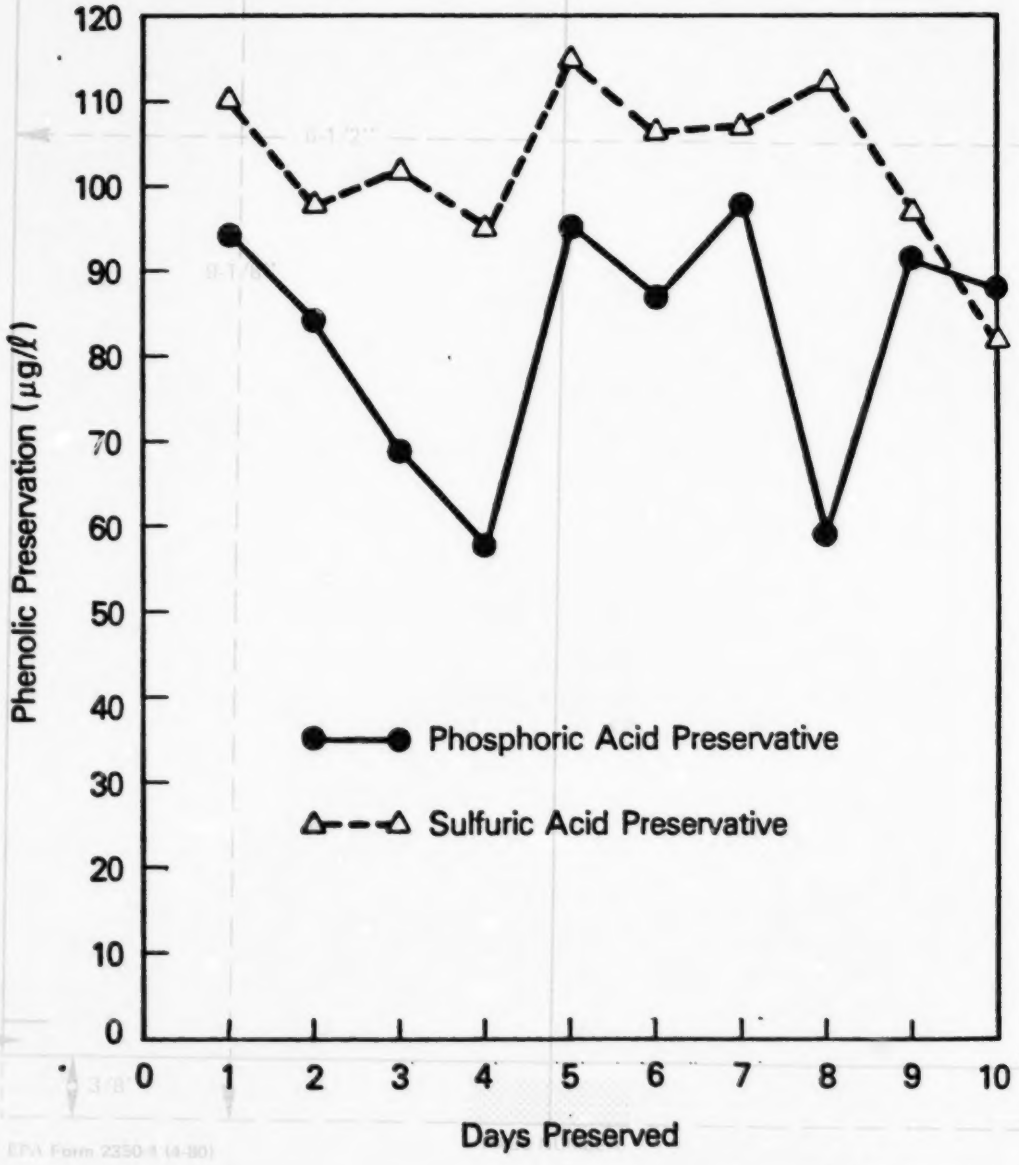


Figure 13

Phenolic Preservation Study

Sample 3313 001 7

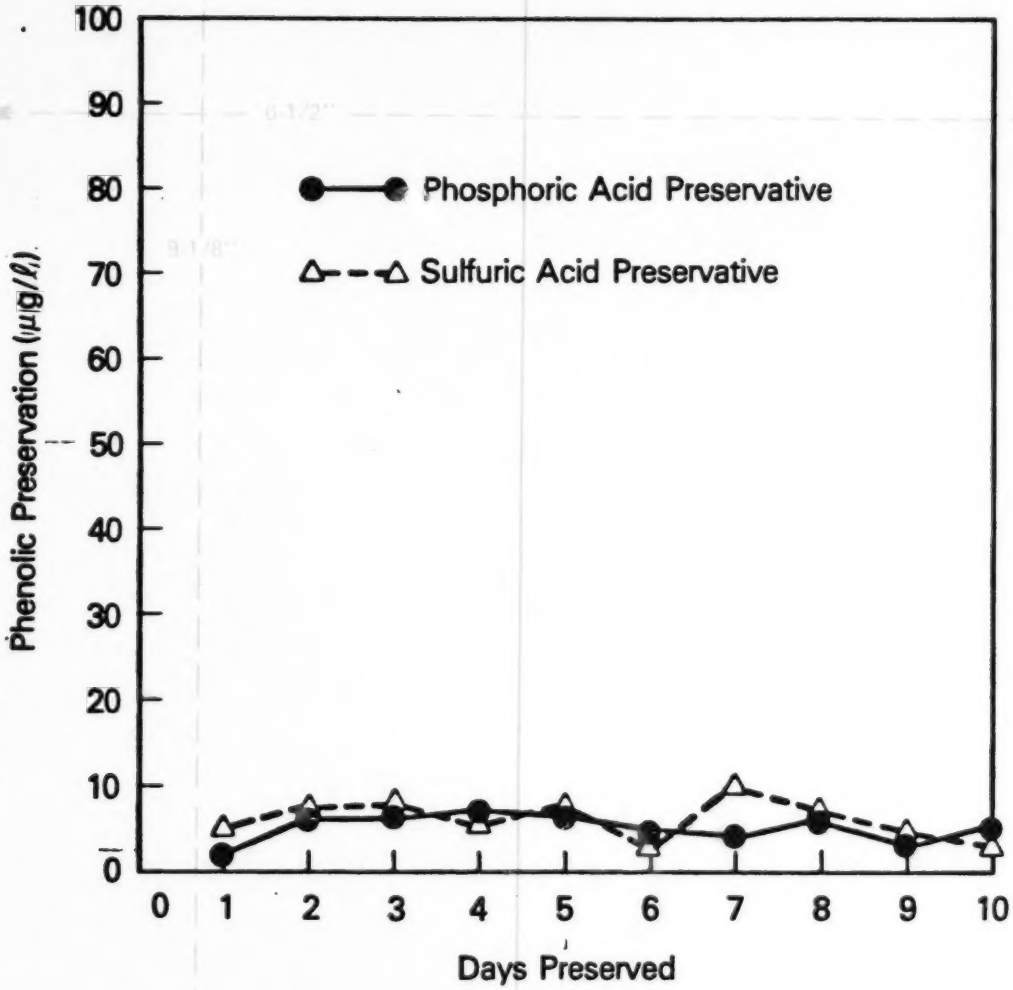
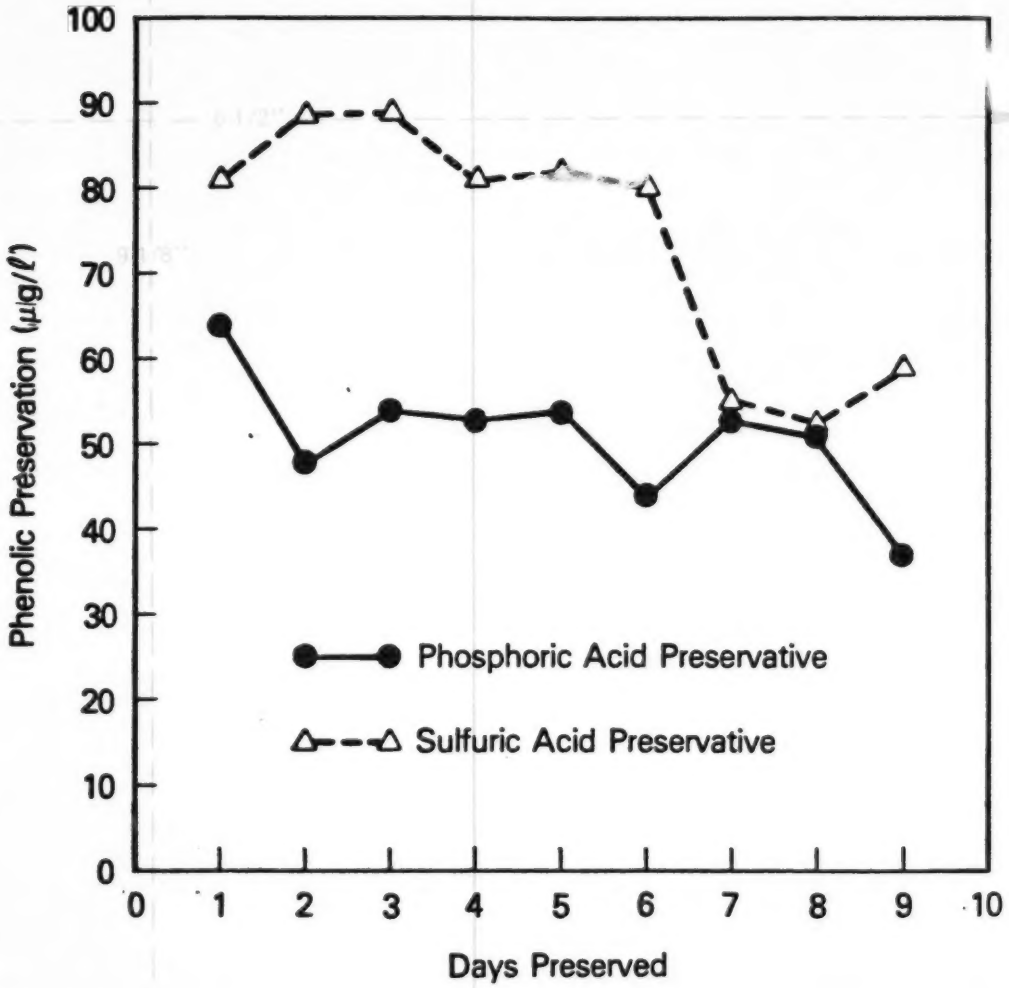


Figure 14

Phenolic Preservation Study

Sample 3861 003 7



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